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CHEMICAL COMBINATION AMONG METALS

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CHEMICAL COMBINATION AMONG METALS

BY

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PREFACE.

The subject of chemical combination among metals is of considerable interest and importance in general chemistry. Viewing the recent developments of the chemistry of metals, we cannot fail to remark the immense strides made in little less than a score of years. This progress has been made possible by the rapid and incessant development of modern metallography. To give a historical picture would involve the detailed discussion of almost all the problems around which metallography is grouped.

The chemistry of metals has been largely studied by means of thermal analysis, and it may be fairly said that the subject has only acquired clearness since the introduction of Tammann's thermal method, dating from the beginning of the present century and still growing steadily in value and importance. In our treatment of the subject of the capacity of metals for combination with each other this method of investigation will be outlined.

The groundwork of any treatise which aims at explaining the nature of chemical combination among metals must be that part in which are described the various states of equilibrium which can be examined by quantitative methods and are, in consequence, susceptible of scientific interpretation. The foundation of the various methods used for defining the conditions of thermal equilibrium is Gibbs' Phase Rule.

In the development of our subject we shall proceed, after a brief account of the various types of equilibrium diagram for binary systems, to define the nature of intermetallic combination. This is a matter of considerable difficulty but of great

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interest. With it is bound up the question of chemical compounds of variable composition, recently thrown into new light by the fundamental work of the Russian chemist Kurnakoff. This part of the subject forms, indeed, a fine memorial to the memory of the great Berthollet, whose figure ever retains the character of modernity. It is the distinctive mark of a genius that he anticipates by many years the developments of philosophic or scientific thought and leaves, thereby, a deep mark on the hard rocks of science —a safe guide to succeeding generations.

There has been a lack, up to the present, of a complete collection of all the binary systems in which intermetallic chemical compounds appear. The chapters on "Homopolar intermetallic compounds" and "Heteropolar intermetallic compounds" now fill this gap. All the studies made up to 1915 have been collected and every system has been discussed, above all, with reference to the various phases of equilibrium which are observed in the fusion of metals.

With this latter account one may say that the development of the work is complete. A short chapter at the end on ternary combinations gives an idea of this as yet little-known field of research. So far the investigations on ternary combinations are few in number and not even completely worked out, but they are enough to claim the attention of the student of this branch of the chemistry of the metals.

An experimental contribution attempts at an investigation of the degree of dissociation of intermetallic compounds, a subject hitherto untouched, but which serves to give a clearer interpretation of the nature of these combinations. Mendeléjeff's and Meyer's classification of the elements, together with the thermal method, have afforded a safe guide in the development of the subject.

The subject of chemical combination among metals has been considerably elucidated by the application of physical methods to the study of metallic alloys. A complete, though summary, description is therefore necessary of the

physical properties of those alloys in which chemical compounds are formed. This task has also been attempted.

An extended historical account of the subject has not been traced for various reasons. Above all, this branch of chemistry is still rather *in fieri* than *in esse*, and is not complete in its various branches. In addition, an account of the development of metallography would be needed, which has already been ably traced elsewhere.[1] We have, therefore, in the chapter on the nature of intermetallic compounds, preferred to confine ourselves to the purely chemical side of the history of the subject.

M. AND C. GIUA.

[1] Guertler, *Metallographie*, Vol. I., Part 1a, 1912. Desch., *Metallography*, 1910.

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ABBREVIATIONS FOR PERIODICALS, ETC. CITED.

Amer. Journ. of Sci.	*American Journal of Science.*
Ann. Chem.	*Liebigs Annalen der Chemie u. Pharmacie.*
Ann. Chim. Phys.	*Annales de Chimie et de Physique*, Paris.
Ann. d. Phys.	*Annalen der Physik.*
Arch. Pharm.	*Archiv der Pharmacie.*
Ber.	*Berichte der deutschen chemischen Gesellschaft.*
Bull. Soc. Chim.	*Bulletin Société Chimique de Paris.*
Bull. Soc. d'Encour.	*Bulletin Société d'Encouragement*, Paris.
Crelles Journ.	*Crelles Journal, Journ. für die reine und angewandte mathematik.*
Chem. Zentr.	*Chemisches Zentralblatt*, Berlin.
Chem. News	*Chemical News*, London.
C. R.	*Compts rendus de l'Academie des Sciences*, Paris.
Dingl. Polyt. Journ.	*Dinglers polytechnisches Journal*, Berlin.
D. R. P.	*Deutsche-Reiche-Patent.*
D. A. or *Drud. Ann.*	See *Annalen der Physik.*
Ferrum	*Ferrum.* See *Metallurgie.*
Gazz. Chim. Ital.	*Gazzetta Chimica Italiana*, Rome.
Génie Civil	*Le Génie Civil*, Paris.
Gilb. Ann.	*Annalen der physik u. der physikalischen Chemie.*
Int. Z. f. Metall.	*International Zeitschrift für Metallographie.*
Jahr. ber.	*Jahresberichte der Chemie.*
J. Am. C. S.	*Journal of American Chemical Society.*
Journ. Ch. Phys.	*Journal de Chimie Physique*, Geneva.
J. C. S.	*Journal of the Chemical Society*, London.
J. de Phys.	*Journal de Physique*, Paris.
Journ. of Phys. Chem.	*Journal of Physical Chemistry.*
J. Russ. Phys. Chem. Soc.	*Journal of the Russian Physico-chemical Society*, Petrograd.
Journ. of Science	See *Philosophical Magazine.*
Journ. prakt. Ch.	*Journal für praktische Chemie.*
Journ. Soc. Ch. Ind.	*Journal of the Society of Chemical Industrie*, London.
Mem. Ist. Lombardo	*Memorie del R. Istituto Lombardo di Scienze e Lettere, Milan.*
Metall.	*Metallurgie.*
Mon. f. Ch.	*Monatshefte für Chemie.*
Mon. Scient.	*Moniteur Scientifique*, Paris.
Nature	*Nature*, London.
Nuovo Cimento	*Il Nuovo Cimento*, Pisa.
Phil. Mag.	*Philosophical Magazine*, London.
Phil. Trans.	*Philosophical Transactions of the R. Society of London.*
Phys. Zeitschr.	*Physikalische Zeitschrift*, Leipzig.
Pogg. Ann.	*Annalen der Physik u. Chemie.*
Proc. Inst. Mech. Engin.	*Proceedings Institute Mechanical Engineering.*
Proc. Roy. Soc. of London	*Proceedings of the Royal Society of London.*
R. Acc. Lincei	*Rendiconti della R. Accademia dei Lincei, Rome.*
Rec. P.-B.	*Recueil des Travaux Chimique des Pays-Bas*, Amsterdam.
Rend. Acc. Scienze Fis. e Nat. Napoli.	*Rendiconti Accademia Scienze Fisiche e Naturali*, Naples.
Rend. Soc. Chim. Ital.	*Rendiconti Società Chimica Italiana*, Rome.

Rep. Brit. Ass.. . . .	*Report of the British Association for the Advancement of Science*, London.
Rev. de Métallurgie . .	*Revue de Métallurgie*, Paris.
Rev. Génér. des Sciences . .	*Revue Générale des Sciences*, Paris.
Trans. Royal Soc. of London . .	*Transactions of the Royal Society of London.*
Verh. K. Ak. Wetensch. Amsterd.	*Werhandelingen der Koning. Akademie van Wetenschappen*, Amsterdam.
Wied. Ann.	*Annalen der Physik* (Wiedemann).
Zeit. anorg. Ch. . . .	*Zeitschrift f. anorganische Chemie.*
,, *Elektroch.*. . . .	*Zeitschrift f. Elektrochemie.*
,, *f. angew. Ch.* . . .	*Zeitschrift f. angewandte Chemie.*
,, *f. Kryst.*	*Zeitschrift f. Krystallographie.*
,, *phys. Ch.*	*Zeitschrift f. physikalische Chemie*

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CHEMICAL COMBINATION AMONG METALS.

CHAPTER I.

Equilibrium Diagrams.

Binary Equilibria.

The application of the principles of the Phase Rule to binary systems may now be regarded as almost completely elaborated. All the forms of diagram theoretically possible have been discussed, and the examples experimentally studied have not only corroborated theoretical deductions, but have enlarged our view of the subject. The knowledge which we possess of the Phase Rule, as applied to the study of two-component systems, serves as a guide and help in the interpretation of phenomena not only of theoretical but also of practical importance.

All the phenomena encountered in the theoretical and experimental study of binary systems may be grouped, according to Roberts-Austen, into three general classes.

Class I.—*The two components form neither chemical compounds nor solid solutions.*

Class II.—*The two components form chemical compounds.*

Class III.—*The two components form solid solutions.*

This classification has a purely systematic value, because in reality there are cases in which the components form solid solutions to a limited extent and in which, while chemical combinations occur, polymorphic transformations exist with more or less extended series of mixed crystals and partial lack of miscibility.

We may allude to other cases encountered practically: for instance, the two components may be completely immiscible in the fused state or only miscible to a limited degree. The schematic reduction to a few types is necessary and sufficient for the interpretation of the different equilibrium diagrams. For our purpose the second and third classes

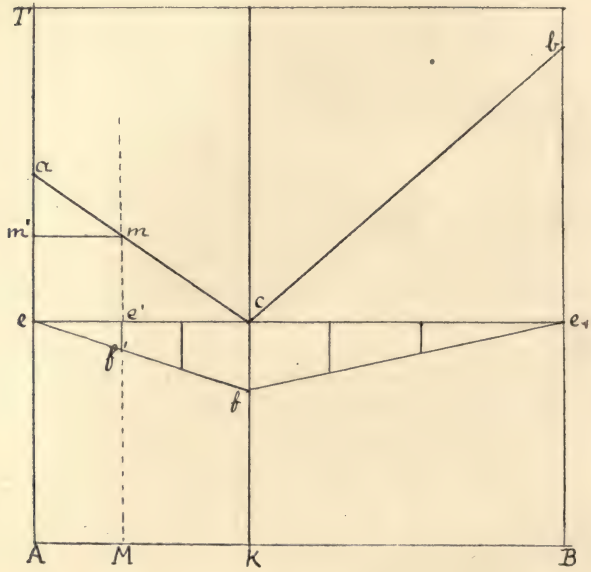

FIG. 1.

alone have a direct importance; but to make the treatment of the subject complete we shall describe all the cases outlined above.

CLASS I. (a) *The two components form neither chemical compounds nor solid solutions.*—This case is quite simple. The possible form of equilibrium is shown in Fig. 1. Each of the two components *A* and *B* lowers the melting point of

the other so that the curve has two branches meeting in the point c, the so-called eutectic point. This point always lies below the melting points of the components. The liquid phase exists in the region above the line $a\ c\ b$, the liquidus curve as it is commonly called. The solid phase exists below the line. In the region $a\ c\ e$ the pure component A separates out; in the region $b\ c\ e_1$ the pure component B separates out. In the region $e\ c\ A\ K$ the pure component A exists together with the eutectic alloy, while in the region $e_1\ c\ B\ K$ the pure component B exists together with the eutectic alloy.

The phenomena which occur on the solidification of fused mixtures of A and B are clearly deduced from the diagram. Let us image a fused mixture of composition represented by m. On cooling, the pure component A will separate out at m and a thermometer immersed in the mixture will show slackening in the cooling curve at the temperature represented by that point.[1] When the mixture cools eventually to the point e', the eutectic alloy separates out. This separation is indicated by a further thermometric arrest proportional to the content in eutectic alloy of the mixture and represented by $e'\ f'$.

A fused mixture of composition K, corresponding to that of the eutectic alloy, solidifies at the eutectic point c. Here the thermometric arrest is greater than that for all the other possible mixtures of A and B, and is represented by the line $c\ f$. The region $e\ f\ e_1$ represents the eutectic arrests for all the mixtures comprised in the diagram.

It should be noted that at the point c the eutectic mixture does not solidify homogeneously but is made up of two components. If a homogeneous phase solidified at c, it would be a compound, not a mixture. The composition of the eutectic alloy does not correspond to any simple molecular proportion of the components, or if it does, it is quite

[1] The withdrawal of A from the melt will alter the composition in the direction of B and thus the temperature will fall until the eutectic point is reached, when the remaining mixture of eutectic composition will solidify.

fortuitous. The position of the eutectic point depends almost always on the melting points of the two components, as has been noted by A. Miolati.[1]

Class I. (b) *The two components are partially soluble in the liquid state and do not form compounds.*—This case, which

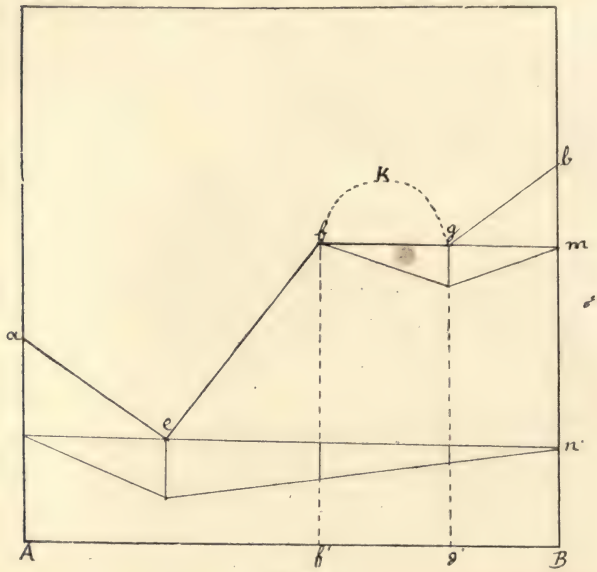

Fig. 2.

occurs in certain pairs of metals, is fairly common among organic and inorganic compounds. The typical case is that of ether and water. The first investigation on organic substances partially soluble in water is that of Alexéjeff,[2] who showed that salicylic acid warmed in a closed tube with water, in which in the cold it is partially soluble, mixes

[1] *Zeit. phys. Chem.*, **9**, 649 (1892).

[2] *Journ. prakt. Chem.*, **133**, 518 (1882); *Bull. soc. chim.*, **38**, 145 (1882); *Wied. Ann.*, **28**, 305 (1886).

with it in all proportions. He has been able to establish the fact that between liquids which only mix in limited proportions, two solutions are always formed, one of component A in component B, and the others of component B in component A, according as one or the other is present in greater proportion at the saturation point.[1]

The equilibrium diagram when the two components A and B are completely insoluble in the solid state and partially soluble in the liquid state is of the form indicated in Fig. 2, in which the liquidus curve is represented by the curve $a\ e\ f\ g\ b$. The horizontal line $f\ g$ indicates the extent of the gap in miscibility. All the liquid mixtures of composition between f' and g' consist of two liquid strata, namely, the component B and the alloy of composition f'. The process of solidification of mixtures of compositions lying between f' and g' is clearly shown from the diagram. Along the line $b\ g$, the component B is first deposited, while along the line $a\ e$, A is first deposited. Along $e\ f$, B is deposited together with the eutectic alloy.

W. Spring and Romanoff [2] have met this case in the study of the equilibrium diagrams of lead-zinc and bismuth-zinc. Other alloys which show this peculiarity are those of lead-nickel, sodium-aluminium, sodium-magnesium, bismuth-aluminium, etc.

This case has been particularly studied by Tammann.[3]

Class II. *The two components form definite compounds.*—When chemical combination takes place in the fusion of two components the diagram is more complicated ; for our purpose these curves have the greatest importance. The compounds formed may have variable conditions of existence and yet be more or less stable.

We shall reduce to three the types of diagrams in which definite compounds occur without the formation

[1] H. C. Jones : *Elements of Physical Chemistry*, p. 179.
[2] *Zeit. anorg. Chem.*, **13**, 29 (1896).
[3] *Ibid.*, **47**, 293 (1905).

of solid solutions between the compounds and the pure components.

(a) *The compound melts at a definite temperature to a homogeneous liquid.*

(b) *The compound has no definite melting point and partially decomposes on melting.*

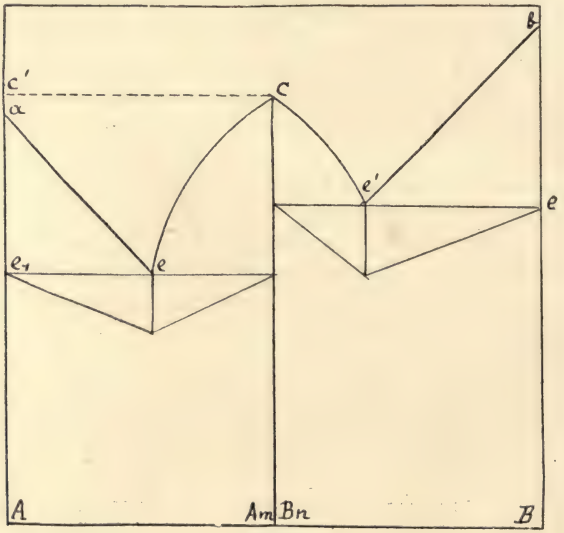

FIG. 3.

(c) 1. *The compound is strongly dissociated in the liquid state.* 2. *The compound on fusion forms two liquid strata.*

(a) Let us imagine a case in which, in addition to the occurrence of a compound with a definite melting point, the three kinds of crystals which exist in the system, *i.e.*, the two components A and B, and the compound $A_m B_n$, are completely soluble in the liquid state and do not form solid solutions. The equilibrium diagram then assumes the form indicated in Fig. 3. This shows three branches, of which

the middle branch $e\ c\ e'$ indicates the conditions of existence of the compound, whose melting point corresponds to the maximum c of the curve. The points e and e' are the two eutectics, e being that between the compound and the pure component A, and e' that between the compound and the pure component B. In the case indicated in Fig. 3, a fused mixture of the components corresponding in composition to $A_m\ B_n$ which is allowed to cool, solidifies homogeneously and completely at the temperature corresponding to c. The fused mixtures of composition e and e' solidify at the temperatures corresponding to those points on the diagram and show maximal thermometric arrests. The thermal phenomena which accompany the solidification of mixtures of intermediate composition can easily be deduced from what has been said above.

Abnormal maxima.—In the study of the antimony-aluminium alloys (*see* Chapter V.) the occurrence of two maxima has been observed, without a corresponding crystalline form in one of the cases. This second maximum is formed, as Tammann has noted[1] by an abnormal process which can be understood from the following considerations. The two components A and B (see Fig. 4) are miscible in all proportions, but the compound, $A_m\ B_n$, forms slowly and separates, after sufficiently long heating, along the line $e\ d\ f$, which is its equilibrium curve. If, however, the melt is not heated long enough, then the formation of the compound $A_m\ B_n$ is not complete, so that, compared to a melt which has been subjected to longer heating, it has a greater content of the two components A and B. The temperature at which crystals of A or B separate out is lower. With an equal degree of heating of the various melts the dotted line $a e_1 d_1 f_1 b$ gives the temperatures at which A, $A_m\ B_n$ and B separate on the respective branches of the curve. If the concentration of the melt has become by the separation of crystals of A or B,

[1] *Zeit. anorg. Chem.*, **48**, 53 (1906).

equal to that indicated by the point e, there will be three kinds of molecules present, namely, A, $A_m B_n$ and B. Since, compared to the velocity with which crystallisation takes place, the velocity of formation of $A_m B_n$ is inconsiderable, then, even with the simultaneous separation of A and $A_m B_n$, the concentration of the melt e will alter until at a lower

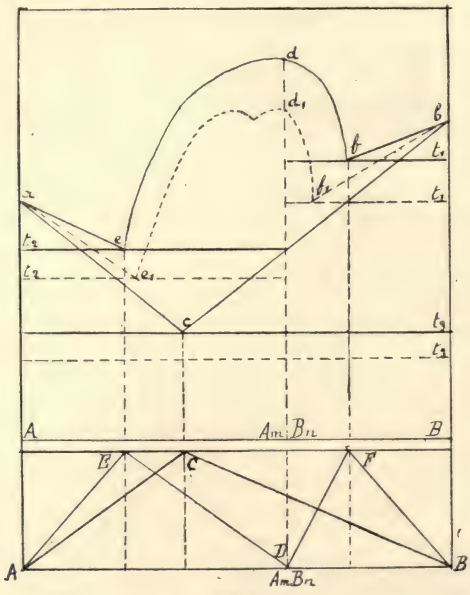

FIG. 4.

temperature than t_3, or about t_3' crystals of B will begin to separate and the remainder will crystallise at a constant temperature with the formation of three kinds of crystals. Melts richer in B will behave in a similar manner on cooling.

Let us consider now the curve $e_1 d_1 f_1$: if with increase of component A the velocity of formation of the compound increases, then the maximum is displaced to d or even a

second maximum is formed. The form that the curve assumes depends always on the duration of the heating of the melt. As has been said, no conclusions as to the composition of a compound can be drawn from the concentration at such a maximum.

If, before the compound is formed in appreciable quantity,

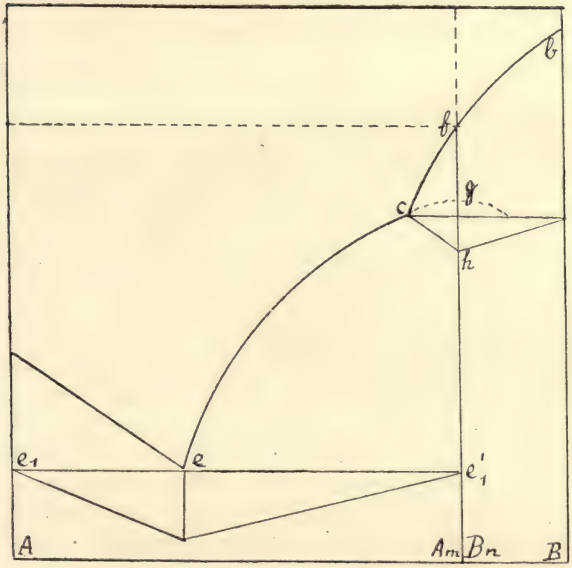

FIG. 5.

the two liquids are immiscible, the phenomena of crystallisation are greatly complicated and do not admit of any quantitative deductions being made.

(b) *The compound has no definite melting point, and decomposes on melting.*—In this case the diagram assumes the form shown in Fig. 5.

As was said above, the compound does not melt to a homogeneous liquid, but at a given temperature decomposes

into a liquid of definite composition and a crystalline portion with a higher melting point, which in the case indicated in the figure is the component B. This process is expressed by the following equation :—

$$A_m B_n \rightleftarrows CB + [(n - c) B + mA],$$
(crystals) (liquid)

in which C indicates the number of molecules of B produced per molecule of $A_m B_n$.

The process of solidification corresponds to the case in which the compound can only exist in the presence of an excess of one of the components. The dotted line which is prolonged from c indicates a region of metastable equilibria and the maximum g corresponds to the composition of the compound. From the diagram we may deduce the thermal phenomena which accompany the solidification of mixtures of varying composition. It is worth while noticing the changes which accompany the cooling of a melt of composition $A_m B_n$. The solidification begins at f, at which temperature the pure component B separates. The separation of B continues until the temperature has fallen to that of the horizontal through c, below which the compound can exist without decomposition. Here the separation of B ceases and the separation of the compound begins with a thermometric arrest corresponding to the distance between h and the horizontal. This arrest does not indicate the formation of an eutectic, but of the compound. The thermometric arrest is proportional to the quantity of the compound which is formed for a given quantity of mixture.

Tammann,[1] who has discussed particularly the phenomena of crystallisation which occur in the type of system just described, states that thermal analysis can safely be applied only when the following conditions are satisfied.

1. The reactions which occur in the melt before and after crystallisation must occur fast enough to keep pace with the process of crystallisation.

[1] *Zeit. anorg. Chem.*, **45**, 24 (1905).

2. The quantity which crystallises in unit time should depend solely on the quantity of heat yielded up by the crystallising mass.

The phenomena of crystallisation are still more complicated if the compound splits up into a definite melt and another compound of different composition.

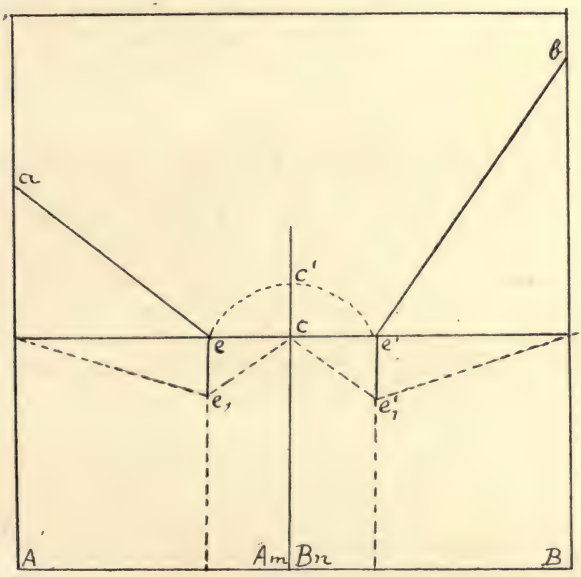

FIG. 6.

(c) 1. *The compound is strongly dissociated in the fused state.*—A particular case which in many respects resembles the one just examined is that indicated in Fig. 6. The maximum c' which indicates the compound does not exist in reality, being flattened out to c. But this temperature corresponds simply to that of the two points e and e', which are the two eutectics—one between the component A and the compound, and the other between the component B and the

compound. The solidification of a mixture corresponding to the composition of $A_m B_n$ is accompanied by a transformation at c where the compound separates. The solidification of the melts corresponding to the two eutectics takes place at the same temperature, but the arrests in these cases are indicated by $e\ e_1$ and $e'\ e'_1$ respectively.

The equilibrium diagram of the system magnesium-aluminium, in which Mg_4Al_3 occurs as a compound, approximates to this, but a perfect example has not yet been encountered in binary intermetallic systems. Such types have, however, been noted in certain organic binary equilibria.[1]

2. A very interesting case is that of a compound which forms on melting two layers miscible with each other at a higher temperature. The diagram in this case is referable to the simplest type shown in Fig. 7. Applying to this diagram the reasoning developed in the preceding cases, its structure is perfectly clear. The eutectics between the compound and the components are e and e'. Along the line $a\ e$ the pure component B separates. The horizontal tract $M\ N$ deserves special notice. During the fusion of the mixtures of compositions between M and N, two liquid layers are formed, so that the compound under certain conditions can exist in equilibrium with the two components. Within the curve $M\ k\ N$ the two liquids exist in a form similar to the well-known emulsions of the organic chemist; but above this curve they mix, forming a homogeneous liquid. The mixture of composition k, which corresponds to the compound $A_m B_n$ in composition, shows a maximal arrest which, according to the considerations already put forward in preceding cases, is not to be attributed to the formation of an eutectic.

The liquidus curve is $a\ e\ M\ N\ e'\ b$. The quantities of liquid which crystallise at the temperatures t_1, t_2, and t_3

[1] *Cf.* R. Kreemann: *Mon. f. Chem.*, **25**, 1215 (1904); **29**, 877 (1908); J. P. Wibaut *Rec. P.-B.*, **32**, 244 (1913). M. Giua, *Ber.*, **47**, 1718 (1914); *Gazz. chim. ital.*, **45**, I., 339, II., 348 (1915).

respectively from equal quantities of homogeneous melts are represented by ordinates in Tammann's diagram.[1] The greatest quantity is given by the liquid which crystallises at t_1 at the composition of the compound, while the quantities

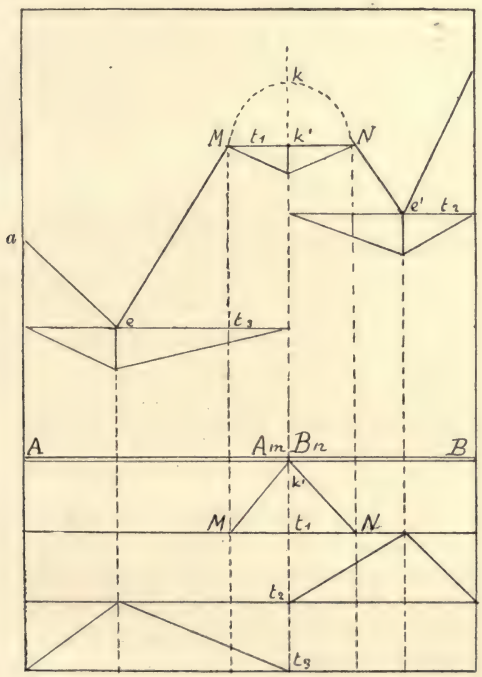

FIG. 7.

which crystallise at t_2 and t_3 become nil for the composition of the compound. The duration of crystallisation also depends on the composition of the melt. There are thus three modes of determining composition. In this type the horizontal line $M\,N$ may be supposed to culminate in k'.

[1] *Zeit. anorg. Chem.*, **47**, 296 (1905).

A sodium-zinc compound of the formula $NaZn_{11}$ is of the type just described.

Class III. *The two components form solid solutions.*—The diagrams which represent the curves of crystallisation of binary mixtures where solid solutions occur have been described and assembled into five types by Bakhuis Roozeboom.[1] The five types of solidification have been divided into two groups according as they show partial or total miscibility. Although Roozeboom's types taken singly do not include the case of the formation of definite compounds, yet they are of great interest because one can often verify the fact that compounds resulting from two components form mixed crystals between more or less wide limits.

In the first group are comprised the types I, II and III, in which complete solubility exists between the two components in both the liquid and the solid states; in other words the fused components solidify forming a continuous series of mixed crystals.

Types IV and V form the second group; in these, the components are only partially miscible in the solid state.

Type I. *The two components form a continuous series of mixed crystals.*—They are completely miscible in the liquid and solid state, and form crystalline masses in which the components are not separate but homogeneously built up. The equilibrium curve assumes the form of Fig. 8. In this, the component *A* lowers the melting point of component *B*, while the latter raises the melting point of the former. No maximum, therefore, occurs in this diagram. Three regions may be distinguished in the diagram: (1) that of homogeneous liquid, (2) that lying between the liquidus curve and the solidus curve, and (3) that below the solidus curve in which homogeneous mixed crystals occur.

A melt of composition *a*, if cooled, deposits mixed crystals of composition *b*, and thereby becomes richer in the com-

[1] *Zeit. phys. Chem.*, **30**, 385 (1899).

ponent A. Consequently, from the same melt there will separate along the curve $b\ c$ a series of mixed crystals increasingly richer in A. The curve $a\ c$ gives the composition of the corresponding melts.

If it be desired to know the relative amount of mixed

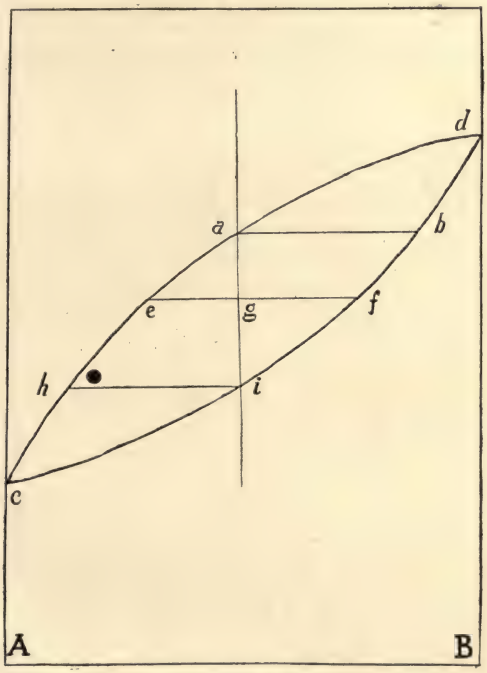

FIG. 8.

crystals formed from a mixture of composition s at a temperature t_1, it may be readily found from the diagram. If a line $e\ f$ be drawn horizontally through t_1, then e will indicate the composition of the fused liquid and f will indicate the composition of the mixed crystals. But the average composition will be represented by g, and therefore

$$x = \frac{\text{weight of mixed crystals}}{\text{weight of fused mixture}} = \frac{g\,e}{g\,f},$$

a relation which holds for melts and mixed crystals following the lines $a\,h$ and $b\,i$ respectively. In the vicinity of the line $h\,i$ the residual liquid is almost nil and the alloy consists almost entirely of mixed crystals.

Several alloys of gold, copper and iron belong to this type.

Type II. *The fused mixtures deposit a continuous series of*

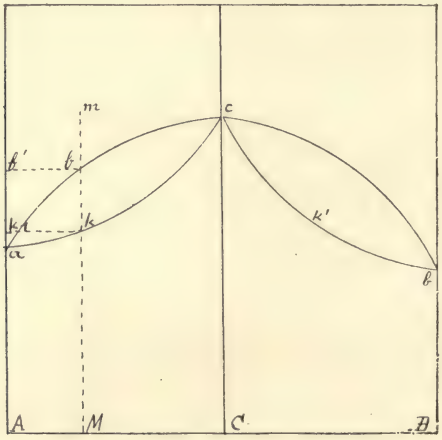

Fig. 9.

mixed crystals : the curve passes through a maximum.—Each component raises the melting point of the other, as is shown in Fig. 9. In this case the curves are quite simple. The liquidus curve is indicated by $a\,f\,c\,b$ and the solidus curve by $a\,k\,c\,k'\,b$. A mixture of composition M between a and c (or between b and c) solidifies in the temperature interval $f\,k$. The composition of the mixed crystals, as in the preceding type, will differ from that of the liquid. The mixture of composition c has, however, a definite solidification point, and to that extent resembles a simple substance. It is constituted of

homogeneous crystals just as a chemical individual, and appears thus under microscopical examination.

This type of crystallisation has been recognised in the binary system lead-thallium (see Chapter V).

TYPE III. *The fused mixtures deposit a continuous series of mixed crystals ; the curve passes through a minimum.*—Each of the components lowers the melting point of the other. The diagram is indicated in Fig. 10. The considerations

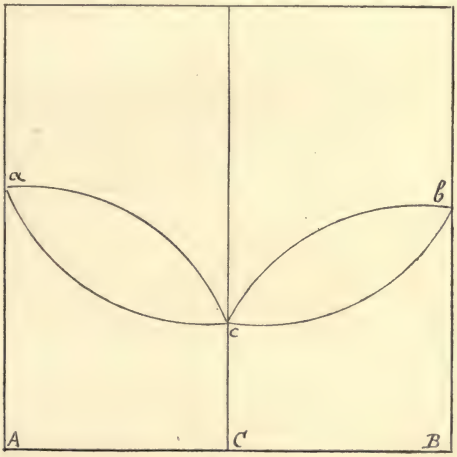

FIG. 10.

put forward in the last case hold in an inverse sense for mixtures of this type. The alloys copper-manganese, copper-gold, nickel-manganese and various others belong to this type.

TYPE IV. *The solidification curve exhibits a transition point.* —This type is shown in Fig. 11. As is seen, component *A* lowers the melting point of component *B*, while the latter raises the melting point of the former. It has already been stated that in this type and the next mixed crystals are not formed in a continuous series. The two liquidus curves are

a c and *b c;* the solidus curves *a d* and *b e* intersect the horizontal through *c* in *d* and *e*. At the temperature of the line *c d e* the melt of composition represented by *c* is in equilibrium with two separate mixed crystals of composition represented by *d* and *e* respectively. At this point there is, of course, a discontinuity. In the solidification of a fused mixture *n*, intermediate in composition between *c* and *d*, mixed crystals of composition n_1 will separate at the point *n*.

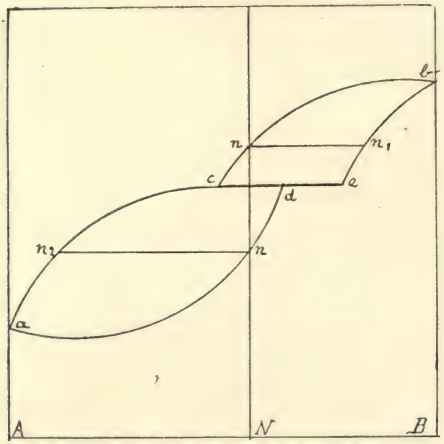

FIG. 11.

Below the point *c* the mixed crystals which separate will lie along the curve *d* n_3 and be in equilibrium with melts lying along the line *c* n_2.

TYPE V. *The solidification curve exhibits an eutectic point.* —Each of the two metals lowers the melting point of the other (see Fig. 12). This type is similar to that described on p. 2. The liquidus curve is shown by *a e b*, the solidus curve by *a f g b*. In the solidification of a mixture of composition *e*, the liquid will be at that point in equilibrium with mixed crystals *f* and *g*. This solidification takes place

at a constant temperature and causes a maximal thermometric arrest.

It will, of course, be quite easy to trace the course of solidification of a mixture *n*: its behaviour will be exactly

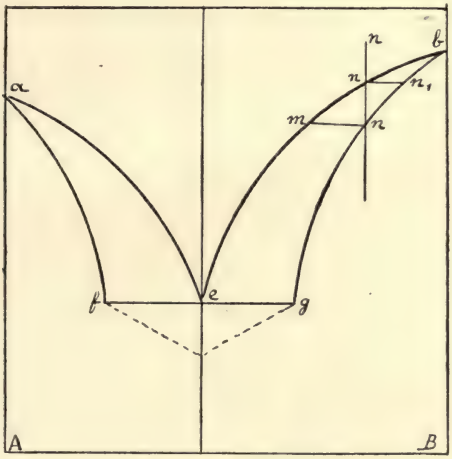

FIG. 12.

similar to that of the mixture considered in Type I (see p. 14).

This type of solidification is fairly common in binary mixtures of metals, as in the alloys copper-gold, nickel-gold, aluminium-zinc, bismuth-lead, and many others.

CHAPTER II.

Thermal Analysis.

If, in the study of equilibrium curves a maximum is found, it may be inferred with considerable probability that a compound has been formed whose composition is indicated by the position of the highest point of that branch of the curve in which the said compound occurs. It is frequently the case, however, that this criterion does not suffice to establish the formation of such a compound, and it is only with the aid of thermal analysis, recently introduced by Tammann, that safe conclusions can be drawn. Tammann's method is based on the interpretation, not only of the first arrests noted in cooling curves (which serve to define the liquidus curve), but also of other arrests due to the solidification of eutectics or to polymorphic transformations within single phases. It is necessary to call attention to the importance of the magnitude of the arrest, which is of course proportional to the thermal change, in thermal analysis. Generally speaking, a maximum thermometric arrest corresponds to the formation of an eutectic alloy ; but this cannot always be inferred. If, for example, at the temperature of eutectic solidification, the separation of a phase occurs, the ordinary thermal changes may not take place and the eutectic arrest may thereby be masked.

The results obtained by thermal analysis are not, then, of absolute value in determining the capacity of two substances to form definite compounds with each other. In the first place, such capacity can only be determined by the thermal method over a range of temperature limited by the conditions of the experiment. There is also a second limitation : thermal analysis studies processes which take

place in heterogeneous systems and cannot take account of processes occurring in homogeneous liquids. In liquid mixtures phenomena are noted concerned with the molecules, which act as crystallisation nuclei. Given the limitation of our knowledge and the theoretical and experimental difficulties which hinder a complete elucidation of the subject, the thermal method is not always sufficient for the solution of a given problem. Recently, however, by the application of physico-chemical methods to the problems of equilibrium new cases have been brought to light and our knowledge has been extended. A classical example is given by the bismuth-thallium alloys. The investigations of this system by M. Chikashigé [1] had given evidence of the existence of a compound of the formula Bi_5Tl_3; but recent researches of Kurnakoff and his collaborators [2] on the fusion curves and electrical conductivity have demonstrated the existence of a γ phase which occurs between 55 per cent. and 64 per cent. (atomic) of bismuth. This phase exists perfectly independently, but cannot be fitted into any of Roozeboom's types for solid solutions. Further, microscopic examination showed that it undoubtedly possessed the characteristics of a chemical compound. According to Kurnakoff, Chikashigé's contention that there exists a compound Bi_5Tl_3 capable of forming solid solutions with excess of thallium or bismuth is not admissible, because the singular points noted do not correspond to the limits of the compound's existence. We shall have occasion to return later to this case, which constitutes a clear case of a chemical individual which does not obey the law of definite proportions.

The phenomena observed in the cooling of a liquid substance are well known, as also the course of the cooling curve of two or three substances fused together; the phenomena differ according to the degree of miscibility in the solid and liquid states. All these cases have been sufficiently

[1] *Zeit. anorg. Chem.*, **51**, 328 (1906).
[2] *Ibid.*, **83**, 200 (1913).

discussed. We prefer to confine ourselves particularly to the questions relating to the formation of chemical compounds. The forms of the principal curves have been already described (see Chapter I). As has been said, and as we shall repeat, the mutual behaviour of two substances is comprehensively and completely described by their equilibrium diagram. With changes in the concentration of two substances there are always definite thermal changes from which general ideas can be obtained as to the structure of the solid phase (see p. 20). As we have seen in the foregoing discussion on equilibria, the interpretation of diagrams where compounds occur is often rendered difficult by the appearance of new phases.

Many compounds which have definite maxima are able to form solid solutions with one or both components and between varied limits. Generally, in the diagrams for metals, various phases appear which may render it impossible to interpret rationally the variations of thermal equilibrium. The diagrams representing systems in which compounds occur capable of forming solid solutions with the components are of great importance from the point of view of chemical theory. We shall speak of these in the section on chemical compounds of variable composition.

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CHAPTER III.

The Nature of Intermetallic Compounds.

The Concept of Chemical Combination and the Phase Rule.

The fundamental principles of the Phase Rule and its varied applications in physical chemistry have already been expounded in numerous publications treating of metallography. This is not the place for even an outline of the subject and we shall therefore assume as well known the fundamentals of Gibbs' theory of heterogeneous equilibria.[1]

In dealing with intermetallic compounds, however, whose nature is not yet completely understood and about which considerable differences of opinion exist, it will be well to begin by elucidating a concept which has an important historical significance.

In the development of the natural sciences, since the first realistic efforts of the Renaissance, certain general principles or fundamental concepts have formed the bases on which experimental science has been built up. To confine ourselves only to the matter which concerns us in the development of our subject, the concepts of *element*, *simple substance* and *chemical compound* formed for some centuries the principal subject of chemical investigation, so that all the theories which have held and still hold in science seem intimately bound up with these concepts.

Even in ancient times logical and scientific methods developed securely on the bases of fundamental concepts, although these may have been causes of error. Among these concepts, that of "element" has dominated the greatest philosophic minds from the most remote antiquity.

"*The influence exerted by this doctrine of the elements,*"

[1] Roozeboom: *Heterogenen Gleichgewichte*, Vols. I. and II.

says E. von Meyer,[1] writing of Aristotle and Empedocles, "*together with its philosophic offshoots on all trends of thought was remarkable. All the scholasticism of the Middle Ages was grounded on this assumption, which became the fount of innumerable errors.*" Nevertheless the logical basis of science has remained, as also the idea that matter in all its varied forms is derived from the elements.[2]

For modern chemistry the most important property of chemical compounds is constancy of composition. But now, according to Kurnakoff,[3] the terms *compound* and *individual* have almost the same significance.

It has fallen to W. J. Gibbs [4] to introduce a new fundamental concept, namely, that of *phases, i.e.*, a system of equilibrium formed of homogeneous bodies separated from each other by surfaces. We must attribute an almost absolute individuality to this concept. By means of it, intermetallic compounds, as also many other complexes, organic and inorganic, which remained completely obscure on the basis of older principles, have received a rational explanation.

It should also be mentioned that the concept of *phase* is much wider than that of *chemical individual* in the Daltonian or Berzelian sense, because by it is indicated not only bodies of constant composition but also the important class of solutions and homogeneous bodies of variable composition.

According to the idea first expressed in 1897 by the technical chemist, Fr. Wald,[5] a *chemical individual* repre-

[1] E. von Meyer: *History of Chemistry.*

[2] Meyer also writes of the ancients: "In the concept of chemical combination, also, we occasionally meet opinions diametrically opposed to those of to-day. In those days the formation of a substance from the interaction of other substances was considered as the creation of a new substance and it was considered that an annihilation took place of the substances from which it was derived. In all directions the mind was the slave of theoretical speculations, without rigorous experimental proof. This lack appears clearly evident from the way in which the ancients viewed the numerous chemical phenomena with which they became acquainted either casually or empirically.

[3] *Zeit. anorg. Chem.*, **88**, 109 (1914).

[4] *Thermodynamic Studies*, 1876—78.

[5] *Zeit. phys. Chem.*, **18**, 337 (1895); **19**, 607 (1886); **22**, 253; **23**, 78; **24**, 315 (1897); **25**, 525; **26**, 77 (1898); **28**, 13 (1899).

sents a phase which in a series of equilibrium changes possesses a notably constant composition.

Kurnakoff,[1] holds that this definition gives a new aid to the recognition of a chemical compound. "*The pure naturalistic and logical conception of a phase here coincides with the mathematical conception of a determinate compound. The phase which exists independently would appear to have individual characters and show substantially the manifestations of the ideal complex of atoms which we call a compound. Many definite compounds have been discovered by means of their reactions or from the diagram of their properties; but up to the present they have not been considered as chemical individuals. In order to be able to demonstrate their existence, it has been considered necessary to isolate them in the form of single and independent phases.*"

The first task, therefore, in the investigation of compound systems is that of establishing the genetic relation among existing phases and of classifying the individuals. From this point of view the domain of chemistry comprehends the classification and study not only of compounds of constant composition, governed by the well-known principles of Proust, but also of solutions, till now considered as homogeneous physical mixtures. Under the phase rule they come to be treated by the same logical method.

As far back as 1907, R. Nasini[2] had placed in clear relief the importance of indefinite combinations in physico-chemical research. He says,[3] "*Another important and fertile region of unlooked-for results is that of the study of physical mixtures, of complex combinations, of combina-*

[1] *Zeit. anorg. Chem.*, **88**, 109 (1914).

[2] R. Nasini: *La chimica-fisica, il suo passato, quello che é e quello che si propone.* Padua, 1907.

[3] *Op. cit.*, p. 38. The same concept has been developed by Le Chatelier, who writes: "On account of the clearness which was given to chemistry by the concept of definite chemical compounds investigators have long occupied themselves especially with the study of these bodies. Compounds with variable composition, solid solutions and homogeneous liquids were on the contrary held of small account, although the importance and significance of these bodies in the study of natural phenomena are considerable." *Leçons sur le charbon*, p. 385. Paris, 1908.

tions of indefinite composition, as Guldberg calls them and as Mendeléjeff called them before him. There is no doubt that in the past chemistry has been too exclusively occupied —although to a large extent necessarily—with the simplest chemical species and has taken little notice of solutions or homogeneous mixtures, including solid solutions and the complex combinations which can exist in and be formed from them in various ways. Wherefore it may very reasonably be said that chemistry—even physical chemistry until a few years ago—was the science only of the most simple and stable chemical species. Having regard to the isolated occurrence in nature of such species and their laboratory origin, these are almost rarities and singular cases obtained and isolated with considerable trouble and artifice. Wald said, indeed, that chemistry only studied and made collection of rarities. Physical chemistry, in fact, finally turned its attention to homogeneous and heterogeneous physical mixtures, to the more complex combinations, those of indefinite composition; it has in other words turned to the study of materials which directly and actually present themselves and with which we find ourselves in contact without the preoccupation of attempting to isolate from them simple chemical species."

Without wishing to discuss, for the moment, the value of the new concept of phases introduced into modern physico-chemical investigation, we will only say that it has been and is of indispensable value in the treatment of indeterminate complexes as stated in the judgment of Nasini quoted above.

In the following pages the problem of intermetallic compounds of variable composition will be more particularly discussed.

Intermetallic Combinations of Variable Composition.

Before discussing this important aspect of equilibrium diagrams for binary systems and making any observations of a general character, it may be well to mention that in our

treatment of the subject we include all cases in which the compound or compounds formed can give solid solutions with one or both components over more or less wide ranges of concentration.

The types described in Chapter I relating to the existence, as shown by the equilibrium diagram, of definite compounds, fall according to the extent of the series of solid solutions into the different types in Roozeboom's classification as outlined on p. 14. As in the preceding pages, we shall here give some

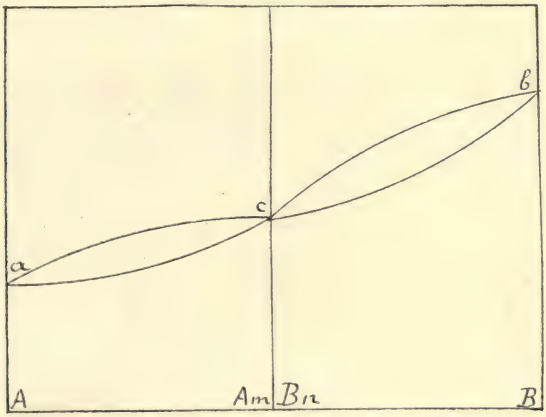

FIG. 13.

indications on the possible interpretation of equilibrium diagrams. The following types will be discussed :—

I. *The compound is completely soluble in its components even in the solid state.*

II. *The compound, which has a definite melting point, forms solid solutions with excess of the components.*

III. *The compound, though forming solid solutions with its components, dissociates on fusion.*

TYPE I.—In this type may be grouped the systems whose diagrams are indicated by Figs. 13, 14, and 15 respectively, according as the melting point of the compound lies between,

below or above the melting points of its components. In the three diagrams the alloys of composition $A_m B_n$ correspond-

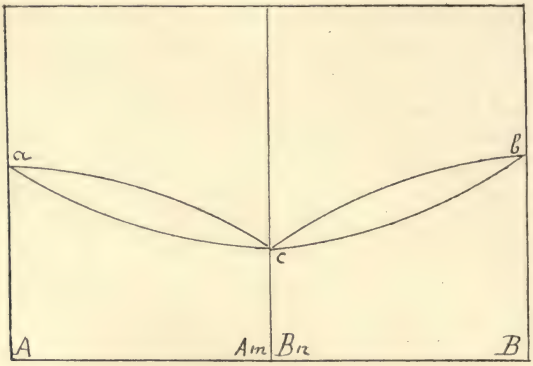

FIG. 14.

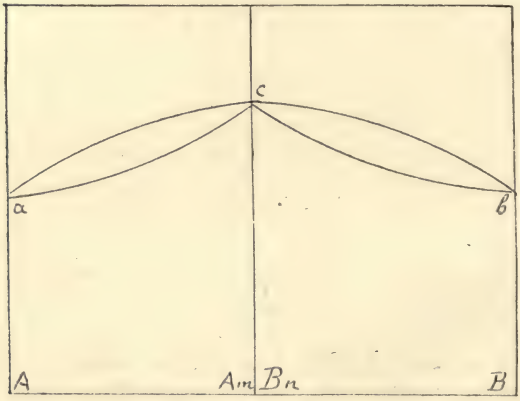

FIG. 15.

ing to definite compounds solidify homogeneously at the point c. For alloys lying between a and c or b and c the solidification proceeds as in Roozeboom's first type described on p. 14.

TYPE II.—This is indicated in Fig. 16 and is equivalent to the fusion in juxtaposition of two systems, each belonging to Roozeboom's fifth type.

The considerations developed concerning this type are sufficient to explain all the processes of solidification of

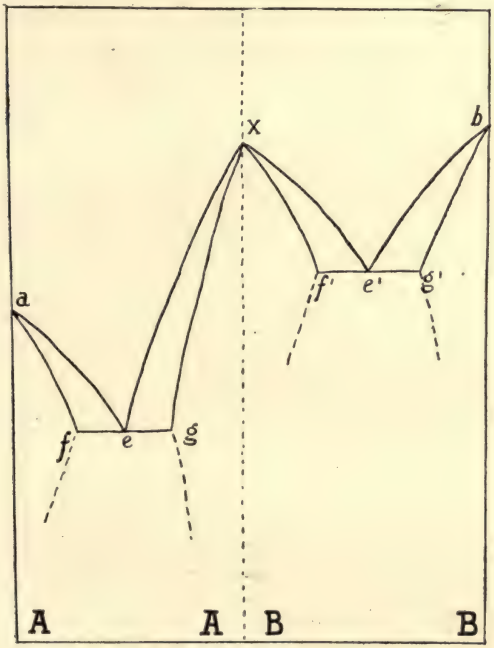

FIG. 16.

fused mixtures whose compositions vary from *A* to *B*. The liquidus curve is represented by the line *a e x e' b* and the solidus curve by the line *a f g x f' g' b*. This type is very common in metallic alloys which form compounds with well-marked melting points. The thermal results have often been confirmed by micrographic analysis. The alloys corresponding to the two eutectics *e* and *e'* are distinguished

by a very characteristic stratified structure; in the region where solid solutions occur, the structure is quite homogeneous. It may be seen, then, from the diagram, how the composition of the solid phase of a compound can vary between limits. As has already been said, solid solutions frequently occur in the formation of compounds, so that generally, the concentration of the liquid or solid phase of a compound is variable, and in such cases the concentration

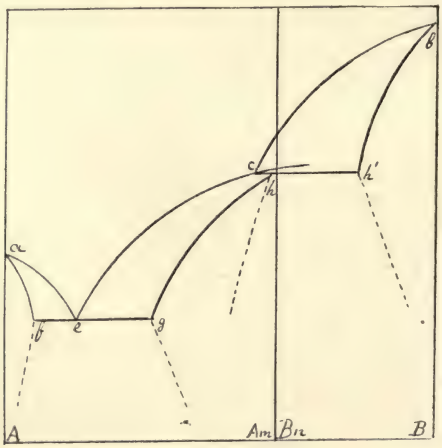

FIG. 17.

corresponding to the maximum of the diagram cannot always serve as a criterion to establish the true composition of the compound. In the later part of the work we shall frequently have occasion to return to this problem, which is becoming of increasing importance. The study of the physical properties of alloys (see Chapter IV) is of great service in the interpretation of those problems for which the thermal method has proved inadequate.

TYPE III.—The diagram is shown in Fig. 17. The liquidus curve is given by the line *a e c b* while the solidus curve is

given by *a f g h h' b*. From the diagram the processes of solidification along *a e*, *c e* and *c b* become quite clear. The alloys from *c* to *h'* in which the compound $A_m B_n$ is formed have very complicated crystallisation processes, because the compound does not actually exist as such even in the solid state, being split up into conjugate solid solutions. The systems silver-antimony, silver-tin and various others belong to this type.

The recent developments of the thermal method and of physical methods in general, which are of such service in the investigations of modern metallography have led various investigators to give a scientific value to the idea of the existence of compounds of variable composition or *indefinite compounds*, an idea championed by Berthollet in his classical dispute with Proust on the limits of chemical combination. Berthollet foresaw clearly this unknown realm of science[1] and asserted that "*compounds which are formed with slight contraction can be found in all proportions and their composition is only limited by their capacity for saturation. Thus, alloys, glasses and minerals are formed in diverse proportions in which occasional gaps occur.*"

Avogadro also, who was an admirer of Berthollet, quickly recognised the importance of such indeterminate compounds in chemical theory. Guareschi in his work on Avogadro[2] has given evidence of the breadth of view of the great

[1] C. L. Berthollet: *Essai de Statique Chimique*, I., 373 (1803).

[2] I. Guareschi: *Opere scelte di Amedeo Avogadro*. Turin, 1911. In the critical and historical discourse introductory to the literature of Avogadro's works, Guareschi writes (p. cix.), "Avogadro was disposed to admit Berthollet's ideas on chemical combination in indefinite proportions. Naturally, he believed in the definite proportions in which gases combined; yet he believed that in certain cases the ideas of Proust and Dalton could be reconciled with those of Berthollet. At the end of his classical memoir (*J. de Phys.*, 1811, LXXIII., pp. 58—76) he writes, 'If we consider the approach of molecules in solid or liquid bodies, when the spaces between the integrating molecules are not of the same order as those between the elementary molecules, combinations may occur in complicated proportions, but these combinations are of a different nature; this idea may serve to reconcile the ideas of Berthollet with the theory of fixed proportions.' These ideas are entirely modern and the work on colloids has rendered this kind of combination very probable."

Piedmontese physicist and chemist. Guldberg,[1] in 1870, recognised the importance of indeterminate compounds. They have recently received fresh light from the labours of Fr. Wald, already noted. The treatment of the matter by this ardent investigator is certainly not the most adapted to throw into relief the importance of the subject of indeterminate compounds because he has attempted to extend to all branches of chemistry particular concepts which have only a limited application, seeking, in fact, to diminish the importance of the atomic and molecular theory—a theory which we may say was born in Italy, first of Avogadro and then of Canizzaro.

R. Nasini [2] has amply dealt with this argument in a notable contribution to which we shall return later, as it has no direct bearing on the present theme.

It is of importance to note that the fundamental principles of chemistry are always essential in the study of compounds of constant composition, but that, naturally, they cannot serve as a guide to the investigation of the indeterminate compounds, whose existence and importance we have indicated. In order to obtain knowledge of this still obscure subject, the principles of the Phase Rule, together with some concepts developed by Fr. Wald, may guide us and give us fresh light. We may record in this connection the contribution of Kurnakoff [3] on the interpretation of equilibria among different phases.

In an equilibrium diagram in which a compound capable of forming solid solutions with its components appears, there is a characteristic which should be noted at once. When the electrical conductivity of these solid solutions is studied, the isotherm shows two branches which intersect in a point corresponding to the maximum on the thermal diagram (see Chapter IV).

[1] Guldberg: *Beitrag zur Theorie der unbestimmten chemischen Verbindungen Ostwald's Klassiker*, n. 139.

[2] *Gazz. Chim. Ital.*, **36**, I., 540 (1906); *ibid.*, **37**, II., 137 (1907).

[3] *Zeit. anorg. Chem.*, **83**, 500 (1913).

The meeting point of two single branches on curves of physical properties is called by Kurnakoff a *singular point* and characterises the composition of a definite compound. This conception, taken from the theory of algebraic curves, is very happy on account of the light it sheds on the question of equilibria among diverse phases. These *singular points*, which are necessary criteria for the determination of compounds in solid or liquid homogeneous media, have been called by Kurnakoff *Daltonian points*, since they illustrate Dalton's law of multiple proportions.

By means of this conception the composition of a definite compound may be indicated. Kurnakoff says,[1] "*It is not the composition of the phase, which is generally variable, but the composition at the singular or Daltonian point which is characteristic on the diagrams showing the properties of a determinate compound. . . . A chemical individual represents a phase which shows singular or Daltonian points on the curves of its properties. The composition which corresponds to these points is the same in all changes of the factors of equilibrium of the system.*"

This definition is not valid for a compound of variable composition, because singular points are lacking on the diagrams of its properties. We shall, therefore, define an indeterminate compound[2] in the following manner:—

"*A chemical individual of variable composition represents a phase which does not show singular or Daltonian points on the curves of its properties.*"

In the description of equilibrium diagrams we shall frequently note the existence of intermetallic compounds of variable composition. In the systems thallium-bismuth and mercury-thallium, such compounds appear; they are more common than is generally believed, for among them may be placed those independent solid phases, indicated in the

[1] *Zeit. anorg. Chem.*, **88**, 109 (1914).

[2] Kurnakoff proposed to term such compounds Berthollides; this denomination, however much an act of remembrance of the great chemist, should not be introduced into use, strictly scientific terms being preferable.

description of binary systems by Greek letters. Such are the phases β, γ and δ of the ferro-silicon alloys and those of copper and silver with tin, cadmium and zinc (see Chapter V).

Intermetallic Compounds and the Theory of Valency (Tammann's Rules).

The description of the behaviour of the elements, which forms the main theme of general chemistry, presents to-day three gaps which will in time be filled as a result of the efforts made to extend our knowledge. These are inorganic complexes, intermetallic compounds, and organic additive molecular compounds. The co-ordination numbers of Werner, illustrated by numerous and careful experimental investigations, have shed considerable light on the inorganic compounds, so that it may be safely affirmed that they constitute the most enterprising attempt at systematisation since the periodic law of Mendeléjeff and Lothar Meyer. The same cannot be said of intermetallic compounds and the molecular compounds of organic chemistry. The ordinary ideas of valency are insufficient in most cases. It is known also that some intermetallic compounds do not conform to the law of definite proportions, thus bringing to life the celebrated dispute between Proust and Berthollet on the limits of chemical combination (compare p. 31).

As Tammann remarks,[1] the theory of valency has given abundant fruit in two great chemical groups, namely, the carbon compounds and the inorganic salts. The latter are, above all, governed by very simple rules in which the character of the element has a relative importance. Regarding, in place of these, the intermetallic compounds, it is seen at once that only a very small minority can be explained on the basis of the known saline valencies of their constituent elements. Tammann may well conclude, therefore, that

[1] *Cf. Lehrbuch der Metallographie, Chemie und Physik der Metalle und ihre Legierungen*, p. 229. Leipzig, 1914.

"Judging from the material at our disposition relating to the binary compounds, it can be maintained that their formulæ, where these compounds are not saline in character, are not generally determined by saline valencies." [1]

Confining ourselves only to a few examples, we will consider two groups of metallic compounds—the amalgams of the alkali metals and the compounds of magnesium and thallium. Lithium, potassium sodium and cæsium form with mercury a complete series of compounds of the type R Hg_2 (where R = alkali metal).[2] Rubidium forms with mercury the compound $RbHg_6$ alone. But besides the series mentioned, which is the most stable, we find the following compounds :—

Li_3Hg	KHg	Na_3Hg	Cs_2Hg
Li_2Hg	KHg_2	Na_5Hg_2	$CsHg$
$LiHg$	KHg_3	Na_3Hg_2	$CsHg_2$
$LiHg_2$	K_2Hg_9	$NaHg$	$CsHg_4$
$LiHg_3$	KHg_9	Na_7Hg_8	$CsHg_6$
		$NaHg_2$	$CsHg_{10}$
		$NaHg_4$	

The behaviour of magnesium is noteworthy because it gives rise to compounds with other metals showing quite distinct melting points. With thallium, magnesium forms the following compounds :—

$$Mg_8\ Tl_3,\ Mg_2Tl \text{ and } Mg_3Tl_2.$$

The compounds formed by mercury with the alkali metals, all more or less stable, are differentiated by their saline character. Mercury, indeed, forms compounds of the type R Hg, but the most stable compounds are those of the type R Hg_2, where the saline valency of the alkali metal cannot hold.

The same considerations may be applied to the compounds which thallium forms with magnesium. It is, perhaps unnecessary to mention that thallium has a double character in its alloys. In its behaviour with sodium and potassium it

[1] Tammann, *op. cit.*, p. 232.

[2] *Cf.* N. S. Kurnakoff and G. J. Zukovsky, *Zeit. anorg. Chem.*, **52**, 416 (1907).

is related to mercury, cadmium, lead and the heavy metals, forming the so-called thallides similar to alkaline mercurides, cadmides and plumbides, but on the other hand it has the property of forming solid solutions with heavy metals such as bismuth, lead, tin, cadmium and mercury.[1]

The foregoing considerations become clear on examining the individual character of metals in their reciprocal compounds.

There frequently exists a certain analogy between the compounds which metals of a sub-group of the periodic system form with another metal, as, for example, in the following series :—

$CuMg_2$	$AgMg$	$AgMg_3$	Cu_2Zn_3	Cu_2Cd_3	$AgCd_3$
$AuMg_2$	$AuMg$	$AuMg_3$	Au_2Zn_3	Ag_2Cd_3	$AuCd_3$
Cu_3Al	$CuAl$	$CuAl_2$	Ag_2Al	Cu_3Sn	Cu_3Sb
Ag_3Al	$AuAl$	$AuAl_2$	Au_2Al	Au_3Sn	Ag_3Sb
$PbPt$	Sb_2Pt	Cu_2Zn_3	Ag_2Zn_3	$AgZn$	$AuSn_2$
$PbPd$	Sb_2Pb	Cu_2Cd_3	Ag_2Cd_3	$AgCd$	$AuPb_2$
Mg_2Sn	Mg_3Sb_2	Tl_3Sb	$SnNi_3$	Sb_2Zn_3	$SbZn$
Mg_2Pb	Mg_3Bi_2	Tl_3Bi	$SnPt_3$	Sb_2Cd_3	$SbCd$
$SbNi$	$NiSb$	$PtSn$			
$SbPd$	$NiBi$	$PtPb$			

But, as Tammann observes,[2] the analogy extends only to any two members of the copper sub-group and makes an exception of the third member.

In chemical combinations the metals, apart from the nature of their saline valency, often unite atom with atom, which shows a certain simplicity in the bonds of atomic forces. The fact noted by Rausch and Traubenberg [3] and mentioned in this connection by Tammann himself that in electrical discharges metallic atoms bear equal quantities of electricity, leads us to regard intermetallic combination as having an electrical nature ; this case would thus be governed by Faraday's second law of electrolysis.[4]

[1] *Cf.* Kurnakoff and Pushin : *Zeit. anorg. Chem.*, **52**, 430 (1907).
[2] *Loc. cit.*
[3] *Phys. Zeit.*, 1912, p. 415.
[4] *Cf.* H. C. Jones : *Elements of Physical Chemistry*, pp. 352, 362.

From the relations among the members of the same natural group of the Periodic System and among the members of different groups, Tammann [1] has enunciated two rules which may be thus stated :—

1. *The elements of a sub-group of the Periodic System do not form compounds with one another.*

2. *An element either forms compounds with all the members of a sub-group or with none of them.*

An exception to the first rule occurs in the combination of bromine and iodine and also in the iron group. But it must be mentioned that this rule has not a general character, as indeed frequently happens in the relations based on the Periodic System. If, for example, we enunciate the rule as follows : *The similar elements of a natural group of the Periodic System do not combine with one another,* several exceptions at once appear. Kurnakoff has found (see Chapter V) that in the first group sodium combines with potassium and may possibly combine with other similar members of that group. Here our knowledge is indeed faulty. In the second group, magnesium combines with zinc, and cadmium with mercury, forming compounds with distinct melting points.

The exceptions to the second rule are more numerous. For example, lead does not combine with copper, nor does it mix in the liquid state ; on the other hand it combines with gold forming two definite compounds ; it mixes readily with silver, but without the formation of a compound—at any rate within the limits of thermal analysis. Thallium combines with mercury, forming a compound of variable composition, but does not combine with zinc or cadmium.

As we have already said, in order to explain the formation of intermetallic compounds it is not possible to make use of the common conceptions of valency and chemical affinity acting between atom and atom. As it is generally

[1] *Zeit. anorg. Chem.*, **49**, 113 (1906) ; **55**, 289 (1906).

necessary in the consideration of molecular compounds to admit the existence of inter-molecular forces, so for intermetallic compounds analogous forces must be postulated, which may be related to the electrical nature of the atoms themselves.

The idea of polar force is not new, since both Berzelius and Mendeléjeff make use of it. It has been largely applied by R. Abegg [1] in the interpretation of variable valency. Nernst [2] also makes a clear distinction between *polar* and *unitary* forces. *Polar* forces depend on the special affinity of the elements for electrons, while *unitary* forces lack this character.

According to Abegg, the valency of an element depends on the nature of the other elements with which it combines. Elements of distinct series in the Periodic System are heteropolar, while neighbouring elements are homopolar. The greater number of intermetallic compounds result from unitary forces and only in comparatively few cases are heteropolar compounds formed. In nature, among the few intermetallic compounds the existence of heteropolar types has been noted (see Chapter IV), and this fact may prove to be useful in elucidating the capacity for chemical combination among metals.

Abegg's theory of valency is of considerable service in the interpretation of molecular complexes. In the contributions mentioned above, a sharp distinction has been made between the normal valency of an element and its counter valency. Assuming on the principles of the Periodic System that the sum of the valencies of an element towards oxygen and hydrogen is equal to 8, Abegg has given the following conspectus of the valencies of the elements comprising the different groups of the Periodic System. In this classification the relation of valencies is as follows :—

[1] *Zeit. anorg. Chem.*, **39**, 330 (1904); **50**, 309 (1906).
[2] *Theor. Chem.*, p. 406, 6th ed., 1909.

Valencies.	Groups.						
	I.	II.	III.	IV.	V.	VI.	VII.
Normal valencies .	+ 1	+ 2	+ 3	± 4	− 3	− 2	− 1
Counter valencies .	(− 7)	(− 6)	(− 5)		+ 5	+ 6	+ 7

Staigmüller[1] arranged all the elements of the Periodic System according to their electrical character; the elements chemically analogous are near to each other, while the elements showing great affinity are remote from each other. The arrangement is as follows :—

H	He	Li	Be	B	C									N	O	F	
	Ne	Na	Mg	Al	Si									P	S	Cl	
A		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se Br
Kr		Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te I
X		Cs	Ba	La	Ce	Nd	Pr										
				Yb		Ta	W		Os	Zr	Pt	Au	Hg	Tl	Pb	Bi	
			Ra		Th		U										

It will be seen that the alloy-forming elements are in the central part of the system, while the extreme members are of heteropolar character to each other and form compounds of a saline nature.

Apart from the property of combination among metals, another character of great importance is their capacity for forming solid solutions. We have already touched on this point in the description of equilibrium diagrams. For further information we refer the reader to the celebrated monograph by G. Bruni: *Feste Losungen und Isomorphismus*, Leipzig, 1908.

The Degree of Dissociation of Intermetallic Compounds.

From the study of the equilibrium diagrams of alloys which form compounds with definite melting points it

[1] *Zeit. phys. Chem.*, **39**, 245 (1902).

appears that the position of the maximum which corresponds to a given compound rarely varies in a uniform manner. This fact is certainly related to the nature of component metals or to their capacity for combination. We have mentioned the rules of Tammann which deal with this capacity for combination on the basis of the position which the individual metals occupy in the Periodic System. But as in related series of intermetallic compounds it is unusual to meet regularity in composition, so also in equilibrium diagrams the region of existence of the new phase-compound is variable. The position of the maximum point of a compound is, in fact, in close relation to its degree of dissociation. When from the diagram there appears a definite region of existence of a compound with a distinct maximum, it cannot always be concluded that the corresponding compound can exist as an independent phase, solid or liquid, at that temperature and concentration. Almost all the intermetallic compounds are more or less dissociated in the fused state. A knowledge of the degree of dissociation is, therefore, of great importance for the subject under discussion, since it is a characteristic property of every intermetallic compound and is, therefore, only definable under determinate conditions. Dissociation in molecular addition compounds can vary between wide limits, but we know very little as yet of the subject and this aspect of intermetallic compounds remains very obscure. The present work constitutes the first attempt to inquire into this important problem.

How can the degree of dissociation of an intermetallic compound be determined ? Here again physical chemistry can give important help. It is known that the melting point or freezing point of any compound, even if more or less dissociated, remains constant if the concentration of the components does not vary ; changes of pressure under ordinary conditions have a negligible effect on the melting point of a substance. We can, then, profit by this experimental fact in the solution of our problem. It is a case, in

fact, for the application of the cryoscopic method to the determination of the degree of dissociation of a compound.

The lowering of the freezing point of water by an electrolyte is always greater than that produced by a non-electrolyte of equal molecular concentration. This fact, as is well known, gives a quantitative basis to Arrhenius' ionic theory —an aspect lacking in the earlier theories of Grotthus, Clausius and Bartoli.

If a molecule is dissociated into two ions the lowering of the freezing point of water is double that which it would be if the molecule were not dissociated ; it is n times greater if the molecule dissociates into n ions. Arrhenius used this fact to determine, by the cryoscopic method, Van't Hoff's constant, i, introduced by him in his wide deductions from the laws of osmotic pressure.

The degree of dissociation a for binary electrolytes is given by the equation—

$$a = i - 1$$

[i is the number by which the expected depression of the freezing point must be multiplied in order to give the actual depression—in other words the number of ions formed by dissociation, per molecule of the electrolyte] and it is known that $i = \frac{t}{1{\cdot}85}$ where t is the observed molecular lowering and 1·85 the lowering of the freezing point by 1 gram molecule of a non-dissociated compound dissolved in a litre of water.

For ternary electrolytes—

$$a = \frac{i - 1}{2},$$

and in general for a substance dissociated into n ions—

$$a = \frac{i - 1}{n - 1}.$$

This law holds for aqueous solutions, and if it could be extended to intermetallic compounds it would be at once

possible to determine the degree of dissociation a. Of necessity, intermetallic compounds cannot be dissociated into ions, but the atoms themselves into which the compounds are split act in the same way.

Adding to a given intermetallic compound a third metal capable of dissolving in it, but not forming solid solutions or combining with either of the components of the compound, there will be a lowering of the solidification point. This will be proportional to the amount of metal as long as the compound is not completely dissociated. If the compound is dissociated, then the point of solidification will be influenced not only by the added metal but also by the components into which it is dissociated, so that it will show a depression greater than that calculated by Van't Hoff's formula—

$$\Delta = \frac{\cdot 02\ T^2}{Q}$$

in which Q is the latent heat of fusion and T the absolute temperature. This formula, at least for low concentrations, permits the calculation of the lowering of the solidification point produced by the addition of a metal to the compound. Such a method allows us to obtain unexpected conclusions as to the nature of intermetallic compounds; it has only been applied so far to a few organic addition compounds.[1]

If a given compound AB breaks up in the liquid state into its components A and B, equilibrium exists when

$$x_1\, x_2 = K\,[100 - (x_1 + x_2)]$$

where x_1, x_2, are the concentrations of A and B respectively and $[100 - (x_1 + x_2)]$ the concentration of the undissociated portion of AB.

If, for example, the compound is dissociated to the extent of 10 per cent. into its components so that $x = x_1 = x_2 = 10$ and $100 - x = 90$, then the constant K at the temperature of fusion is—

$$\frac{100}{90} = 1{\cdot}11.$$

[1] *Cf.* R. Kremann: *Monatshefte f. Chem.*, **25**, 1215 (1904).

In this case in place of 100 moles we have 90 moles acting as solvent; the 20 moles of products of dissociation cause a lowering of the melting point. The melting point, calculating the lowering per 100 moles, is lowered

$$\frac{20 \cdot 100}{110} \Delta$$

below what it would be if the compound were not dissociated.

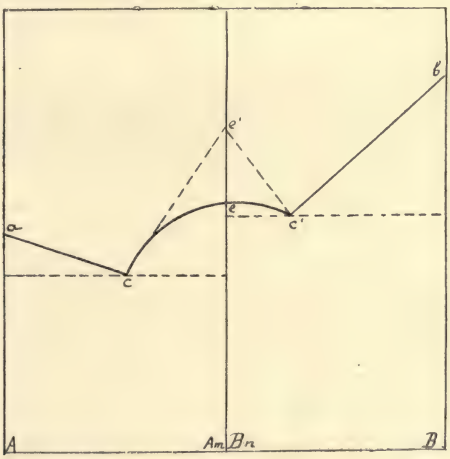

FIG. 18.

This factor must, therefore, be added to the value of Δ which is obtained for the addition of the metal to the compound AB, and which, according to hypothesis, behaves normally in the fused solvent.

Kremann, in the paper cited, has calculated the lowering of the melting point of a pure compound from theoretical and practical considerations with regard to the position of the maximum corresponding to the given compound. In Fig. 18 is shown the solidification curve of two components A and B which give rise to the formation of a compound

$A_m B_n$ which melts at a temperature corresponding to the point e. The compound $A_m B_n$ is formed along the branch of the curve $c\ e\ c'$ and shows a flattened maximum since it dissociates on fusion. If it melted without dissociation, the maximum would be higher, probably at e', obtained by the intersection of the tangents drawn through the eutectic points $c\ c'$. The triangular region $c\ e\ c'\ e'$ is purely hypothetical and does not exist in reality.

Almost all intermetallic compounds have more or less flattened maxima; only certain compounds of magnesium and antimony are formed without a high degree of dissociation.

Kremann's calculated results are given in the following table. In the first column is shown the degree of dissociation of a given compound, the second column K gives the

D	K	a	x	y	δ	D	K	a	x	y	δ
5	0·2632	0	5·00	9·52	2·6	25	8·333	0	25·00	40·00	11·1
		2	4·14	9·68	2·7			6	22·57	39·77	11·1
		6	2·88	10·55	3·0			12	20·45	39·92	11·1
		12	1·86	13·81	3·8			20	17·99	40·56	11·3
		20	1·22	18·51	5·1			35	14·43	42·74	11·9
		35	0·73	26·87	7·5			50	11·87	45·55	12·7
		50	0·52	33·91	9·4	30	12·86	0	30·00	46·16	12·8
10	1·111	0	10·00	18·18	5·0			6	27·65	45·88	12·7
		6	7·57	18·61	5·1			12	25·52	45·85	12·7
		12	5·87	20·14	5·6			20	23·04	46·21	12·8
		20	4·36	23·09	6·4			35	19·17	47·59	13·2
		35	2·83	29·51	8·2			50	16·37	49·72	13·8
		50	2·11	35·65	9·9	35	18·85	0	35·00	51·85	14·4
15	2·647	0	15·00	26·09	7·2			6	32·73	51·53	14·3
		2	14·11	26·03	7·2			12	30·64	51·30	14·3
		6	12·51	26·79	7·2			20	28·13	51·49	14·3
		12	10·51	26·96	7·5			35	24·16	52·38	14·5
		20	8·50	28·79	8·0			50	20·98	53·59	14·9
		35	5·94	33·27	9·2	50	50·00	0	50·00	66·66	18·5
		50	4·47	38·15	10·6			6	48·05	66·30	18·4
20	5·000	0	20·00	33·33	9·2			12	46·13	65·97	18·3
		6	17·53	32·23	9·2			20	43·90	65·48	18·2
		12	15·42	33·63	9·3			35	40·00	65·72	18·3
		20	13·10	35·03	9·6			50	36·00	66·03	18·3
		35	10·00	37·94	10·5						
		50	7·95	41·79	11·6						

equilibrium constant, a gives the number of moles of one component added per 100 moles of compound, x the number of moles of the other component after the change of equilibrium, y the number of moles lowering the melting point, calculated per 100 moles total, and δ the depression of the melting point calculated from the preceding data on the assumption that a change of one mole causes a variation in the melting point of ·278°.

Experimental.

It was desired to determine experimentally the degree of dissociation of the compound formed between bismuth and thallium (see Chapter V), a compound which, according to Chikashigé, has the formula Bi_5Tl_3, while according to Kurnakoff, it belongs to the class of compounds of variable composition. The case presents, therefore, a double interest because, if it were possible to demonstrate experimentally that this compound is more or less dissociated, the methods used by Kurnakoff to affirm the absence of singular points in the equilibrium curve corresponding to the range of existence of the compound may have a relative value applied to the case in point. It was, however, assumed that the compound Bi_5Tl_3 exists. It was prepared by melting together in a Jena glass tube 62·955 gm. of bismuth and 37·045 gm. of thallium. The fusion was made in an atmosphere of hydrogen, because the resulting compound, as well as the components, change quickly in contact with air. The melting point was found to be 211·1°.

To measure the degree of dissociation of this compound, tin was selected, a metal which does not combine with bismuth or thallium, as various workers have shown, and as was verified in the experimental part of this work. If in fact it entered into combination with bismuth or thallium the melting point of the compound would not be lowered by the addition of tin. Tin forms, it is true, solid solutions with bismuth and thallium, but only to a limited degree.

The form of the curve for bismuth-thallium shows that between the limits of validity of the cryoscopic method this capacity should not exert any influence. We record on this point the investigations of Heycock and Neville [1] on the determination of the molecular weight of different metals (including thallium and bismuth) using tin as a solvent.

The determination of the lowering of the melting point of the thallium-bismuth compound was made in a current of hydrogen; the thermometer, divided in tenths of a degree, had been standardised at the Charlottenburg Reichsanstalt (Berlin). For these determinations it is sufficiently accurate to work to one-tenth of a degree.[2]

The whole apparatus consisting of the tube containing the substance together with the thermometer, the electrically-driven shaker and the tube leading the hydrogen from an ordinary Kipp, was maintained in a metal bath (Rose alloy) large enough to ensure a constant and not too rapid lowering of temperature. The results obtained are shown in the following table :—

Weight of thallium-bismuth compound in grams.	Weight of tin, grams.	Tin, per cent.	Δ Found.	Δ Calculated.
33·0549	0	0	—	50·39
,,	0·2314	0·7	51	,,
,,	0·9579	2·89	127·34	,,
,,	1·5170	4·58	158	,,
,,	3·5650	10·78	145·7	,,

It is seen at once how the molecular lowering varies with the addition of tin from a minimum to a maximum value which remains nearly constant. We shall discuss this behaviour later.

[1] *J. C. S.*, **55**, 666 (1889); **57**, 376 (1890).

[2] Tammann in his classical researches used a thermometer divided in tenths of a degree. *Cf. Zeit. phys. Chem.*, **3**, 441 (1889).

The molecular lowering was calculated by Van't Hoff's formula. For this it was necessary to know the latent heat of fusion of the compound, and this was obtained approximately by the method of G. Tammann [1] and W. Plato [2] by examination of the curve of cooling. A mean of five determinations gave 93 cal.

Up to a concentration of about 1 per cent. tin, the compound thallium-bismuth shows an inappreciable dissociation because the molecular lowerings calculated and observed are particularly concordant. With the increase in the content of tin the compound is more and more dissociated, so that at a concentration of 4·58 per cent. of tin the observed value is triple the calculated value—an unforeseen result.

In the application of the cryoscopic method to the determination of the degree of dissociation of an intermetallic compound it was necessary to assume that the addition of an external substance did not influence in any way the dissociation of the compound, and such an hypothesis was all the more plausible since the dissociation in the case in question was not ionic but atomic. The results obtained, however, render this hypothesis untenable since, even at small concentrations, an external substance such as tin can influence notably the dissociation of an intermetallic compound.

The fact that the compound TlBi, corresponding to the γ phase of the system studied by Kurnakoff, shows practically no dissociation renders more clear the deductions of this intrepid investigator with reference to the existence of intermetallic compounds of variable composition.

The compound thallium-bismuth alters rapidly in air ; by the addition of tin it becomes very stable, so that with about 10 per cent. of tin it retains its metallic lustre for a long period.

[1] *Zeit. anorg. Chem.*, **43**, 218 (1905). *Cf.* also Tammann, *op. cit.*, p. 31.
[2] *Zeit. phys. Chem.*, **55**, 721 (1906).

Existence of Intermetallic Compounds in the Vapour state.

Our information as to the vapour tension of intermetallic compounds is not very extensive. H. v. Wartenberg [1] has recently published an interesting investigation in which the problem is given a theoretical basis.

Experimentally the subject presents many difficulties. On the volatility of metals we have the data furnished by G. W. A. Kahlbaum [2] in a notable study of the subject. From this, certain anomalies appear, for example, the low volatility of tin. Among the intermetallic compounds, Berry [3] succeeded a few years ago in showing that the compound $MgZn_2$ distils in vacuo at 600° and H. v. Wartenberg (*loc. cit.*) also studied the vapour tension of the compound Na_3Hg.

The problem of the existence in the vapour state of intermetallic compounds is doubtless in close connection with the affinity relations of the said compounds about which, however, nothing is at present known. As we have already seen in the preceding pages, the bond of valency for these compounds is not very strong; but our observations are confined to the purely qualitative side of the subject.

Admitting this weak bond, we can foresee that many intermetallic compounds which even in the liquid state undergo dissociation to a greater or less, but never negligible, degree, will be strongly or completely dissociated in the vapour state.

The heat of formation of intermetallic compounds must have a considerable influence on their degree of dissociation. It is difficult to obtain data on the existence in the vapour state of compounds which are formed from their elements with considerable evolution of heat.

[1] *Zeit. electro. Chem.*, **20**, 443 (1914).
[2] *Zeit. anorg. Chem.*, **29**, 177 (1902).
[3] *Proc. Roy. Soc.*, A, **86**, 67 (1911).

Arguing from a thermodynamic theorem of Nernst it may be assumed that an intermetallic compound whose boiling point differs by a few hundred degrees from those of its components will have a vapour tension experimentally determinable.

If two monatomic vapours, A and B, combine to form a gaseous compound D, the reaction probably occurs with contraction. Applying Nernst's principle the following is the equation of stability of the compound :—

$$A + B = D + Q + \lambda_A + \lambda_B - \lambda_D,$$

where Q is the heat of formation at constant pressure and λ_A, λ_B, λ_D the latent heats of evaporation of A, B and D respectively. Then—

$$\log \frac{P_D}{P_A P_B} = \frac{Q}{4{\cdot}57\,T} + \frac{\lambda_A + \lambda_B - \lambda_D}{4{\cdot}57\,T} - 1{\cdot}75 \log T - \Sigma \nu C,$$

P_A, P_B and P_D being the partial pressures of the gases T and the absolute temperature.

In this equation, the stability of the compound D increases with increase of the quotient on the left of the equation. The quantity Q may be determined by means of the heat of solution. The latent heats of evaporation may be obtained from Trouton's rule, according to which the molecular heat of evaporation is proportional to the boiling point on the absolute scale.

H. v. Wartenberg found that the gaseous compound $MgZn_2$ is fairly stable at low temperatures but unstable at higher temperatures. The existence of the compound Na_3Hg in the vapour state has been demonstrated.

The fact that some intermetallic compounds can exist in the vapour state, although it does not solve the question of the nature of the linkage which binds together the constituent atoms of intermetallic compounds, offers some prospect of the possibility of explaining such combinations by the principles of the theory of valency. Between saline metallic

compounds and the true mixtures which make up inanimate nature there is no sharp break but rather a gradual transition which modern research has explored in the study of solid solutions and labile combinations (intermetallic compounds, additive compounds, etc.).

CHAPTER IV.

Physical Properties.

Influence exercised by the presence of Intermetallic Compounds on the physical properties of Alloys.

In the preceding pages we have called attention to certain limitations of the thermal method in the complete study of equilibrium diagrams, above all, when it is a question of inferring the formation of one or more compounds. But, in addition to the thermal method, there is opened up a wide field of investigation in the accurate study of certain physical properties of alloys, such as specific volume, thermal and electrical conductivities, hardness, magnetic properties, thermo-electric potential, electrolytic potential, heat of formation, specific heat, microscopic characters and crystalline form.

The presence of compounds always has some effect on the physical properties of alloys. A greater or less degree of discontinuity is often sufficient, not only to corroborate the results obtained by thermal analysis, but also to fill in any gaps which could not be explored by the thermal method alone. For example, the fact, placed in evidence by Kurnakoff, of the existence of intermetallic compounds with irrational maxima (*i.e.* compounds which do not obey Dalton's law of constant proportions) has only been capable of development and interpretation by means of the study of physical properties. According to Kurnakoff, there should be, for every determinate compound, a corresponding discontinuity or singular point in the curve of physical properties and composition. When this discontinuity is lacking, a maximum noted on the curve obtained by the thermal

method would correspond to a compound of variable composition. It is the absence of this discontinuity in the electrical conductivity and compressibility curves in the bismuth-thallium and mercury-thallium alloys which led Kurnakoff (see Chapter V) and, more recently, his pupil P. Paulovitch [1] to postulate irrational maxima in these systems.

In alloys where the formation of compounds does not take place, the physical properties are almost always linear functions of the composition, as in the case of specific volumes, or continuous functions showing maxima or minima, as in the case of the electrical conductivity and hardness of solid solutions.

Specific Volume.

The specific volume of a mixture formed from two components is a linear function of the composition and can generally be calculated from the specific volumes of the single components; it is, in short, an additive property. If x and y are the masses of the two components and v_1 and v_2 their specific volumes, the specific volume of a mixture is deduced easily from the mixture rule :—

$$v = \frac{xv_1 + yv_2}{x + y} = v_1 + (v_2 - v_1)\frac{y}{x + r}$$

or, putting $\frac{y}{x + y} = r$

$$v = v_1 + (v_2 - v_1)\, r.$$

This equation means that in the mixing of the components there is no volume change. This rule is, however, not always strictly valid. Small deviations have been noted in the case of the formation of solid solutions and eutectic mixtures. It must also be mentioned in this connection

[1] *Bull. Soc. Chim.*, (4), **20**, 2 (1916).

that a linear relation can subsist in cases where the components form a continuous series of solid solutions.

The formation of a chemical individual introduces a discontinuity into the curve of specific volumes. If for example the specific volumes of two components which do not combine are plotted for varying concentrations, they will form a straight line; if, on the other hand, a compound appears, the curve will consist of two branches which intersect in a point which, if secondary phenomena do not interfere, indicates the composition of the compound. The case is different where the compound forms solid solutions with one or both of the components; the two lines of the preceding case are then intersected by a third line so that two points are obtained, neither of which correspond to the maximum of the compound. As a rough approximation this maximum can be obtained by producing the two lines till they meet. The point of intersection should give the maximum of the compound.

The following arithmetical rule, deduced by Maey [1] may be applied to a mixture of two compounds resulting from the union of two elements A and B. If x an y are the masses of the two elements in a mixture of the two compounds (1) and (2) formed from the union of the said elements, x_1, y_1, and x_2, y_2, the masses of the elements in the two compounds, then

$$x = x_1 + x_2 \text{ and } y = y_1 + y_2$$

so that

$$\frac{y}{x+y} = \frac{y_2}{x_2+y_2}\,\frac{x_2+y_2}{(x_1+y_1)+(x_2+y_2)} + \frac{y_1}{x_1+y_1}\left(1 - \frac{x_2+y_2}{(x_1+y_1)+(x_2+y_2)}\right)\frac{y}{x+y} = r$$

is the relative amount of the element y, $\frac{y_1}{x_1+y_1} = r_1$ and $\frac{y_2}{x_2+y_2} = r_2$ are the relative amounts of y in the

[1] *Zeit. phys. Chem.*, **29**, 122 (1899)

two unknown compounds, while $\frac{x_2 + y_2}{(x_1 + y_1) + (x_2 + y_2)} = q$ is the relative amount of the compound (2) in the mixture. The relation can be stated as

$$r = r_2 q + r_1 (1 - q) = r_1 + (r_2 - r_1) q_1,$$

or in other words, the relative content of the mixture in one of two elements is a linear function of its content in one of the two compounds.

As a deduction from this simple relation it may be recorded that specific volume can be substituted in the calculation of atomic volume. We may consider, for example, the mixtures of mercury with the alkali metals.

If V_1 be the atomic volume of mercury, V_2 that of the alkali metal in the mixture, n_1 the number of atoms of mercury and n_2 the number of atoms of the alkali metal; and if V be the mean atomic volume of the mixture and R the relative atomic content in alkali metal, then

$$V = \frac{V_1 n_1 + V_2 n_2}{n_1 + n_2} = V_1 + (V_2 - V_1) R$$

$$R = \frac{n_2}{n_1 + n_2}.$$

These two equations can also be obtained from the atomic weights of the elements comprising the mixture. For if M_1 and M_2 be the atomic weights of the elements and m_1 and m_2 their relative amounts in the mixture,

$$n_1 = \frac{m_1}{M_1} \text{ and } n_2 = \frac{m_2}{M_2},$$

and hence

$$\frac{n_1 + n_2}{n_2} = \frac{\frac{m_1}{M_1} + \frac{m_2}{M_2}}{\frac{m_2}{M_2}} = \left(1 - \frac{M_2}{M_1}\right) + \frac{M_2}{M_1}\left(\frac{m_1 + m_2}{m_2}\right)$$

$$\text{or } \frac{1}{R} = \left(1 - \frac{M_2}{M_1}\right) + \frac{M_2}{M_1}\left(\frac{m_1 + m_2}{m_2}\right).$$

For V,

$$V = \frac{V_1 n_1 + V_2 n_2}{n_1 + n_2} = \frac{v_1 M_1 n_1 + v_2 M_2 n_2}{n_1 + n_2} = \frac{v_1 m_1 + v_2 M_2}{m_1 + m_2}$$

$$\frac{m_1 + m_2}{m_2} \cdot \frac{n_2 M_2}{n_1 \ n_2} = v \frac{1}{r} R M_2.$$

Putting $v = a + b\,r$ where a and b are two constants, by substitution

$$V = a M_1 + [M_1 (a + b) - M_1 a] R.$$

From this expression it is seen that V is a linear function of R.

Maey has applied these relations to many alloys, even in some cases where compounds are formed. In the following table we reproduce some values from Maey for alloys which do not show sufficiently great deviations in their specific volumes for existence of compounds to be inferred.

ALLOYS SHOWING CONTRACTION IN SPECIFIC VOLUME.

Alloys.	$v = a + b.p.$	$\Delta v.$	$p.\Delta v.$	$\frac{\Delta v}{v}.$
Bi — Cd	·10181 + ·0001373 p	— ·00015	51·8	— ·001
Ag — Bi	·0955 + ·000063 p	— ·0004	49·0	— ·004
Hg — Sb	·07368 + ·0001422 p	— ·0008	50·8	— ·010
Hg — Sn	·07366 + ·0006345 p	— ·00091	53·7	— ·009

ALLOYS SHOWING INCREASE IN SPECIFIC VOLUME.

Alloys.	$v = a + b.p.$	$\Delta v.$	$p.\Delta v.$	$\frac{\Delta v}{v}.$
Sn — Sb	·13710 + ·0001187 p	+ ·0011	51·4	+ ·007
Sn — Zn	·13710 + ·000010 p	+ ·0005	75·0	+ ·005
Pb — Cd	·08791 + ·0002763 p	+ ·00035	8·3	+ ·001
Pb — Sb	·08791 + ·0006106 p	+ ·00100	54·1	+ ·009

ALLOYS SHOWING BOTH POSITIVE AND NEGATIVE DEVIATIONS.

Alloys.	$v = a + b.p.$	$\Delta v.$	$p.\Delta v.$	$\frac{\Delta v}{v}$.
Bi — Sb	·10181 + ·0004715 p	— ·00013	37·1	— ·001
		+ ·00003	22·7	+ ·0003
Bi — Sn	·10181 + ·0003530 p	+ ·00105	3·3	+ ·010
		— ·00058	62·5	— ·005
Cd — Sn	·11544 + ·0002156 p	+ ·00063	80·5	+ ·005
		— ·00012	14·7	— ·001
Pb — Sn	·08811 + ·0004900 p	+ ·00085	16·0	+ ·009
		— ·00073	69·5	— ·006
Pb — Ag	·08791 + .0000761 p	+ ·00064	11·5	+ ·007
		— ·00043	67·6	— ·005
Ag — Cu	·01591 + ·000176 p	+ ·0007	5·6	+ ·0074
		— ·00003	50·35	— ·003
Au — Cu	·05191 + ·000605 p	+ ·0004	6·8	+ ·007
		— ·00003	1·99	— ·0006
Au — Ag	·05191 + ·0004309 p	+ ·00016	76·5	+ ·002
		— ·00007	12·0	— ·001
Au — Sn	·05191 + ·000852 p	+ ·00108	37·0	+ ·013
		— ·00104	22·7	— ·015
Ir — Pt	·04461 + ·0000190 p	+ ·00011	66·7	+ ·002
		— ·00007	95·0	— ·002

From the study of specific volume concentration curves, Maey[1] has affirmed the existence of the following compounds:—

$SnAg_3$	Sb_2Cd_3	$SuCu_2$	$CuCd_3$
Au_2Bi_3	$SbAg_3$	$CuZr_2$	AgHg
Au_2Pb_3	$SbCu_3$	$AgZn_4$	
Sb_3Zn_2	FeSb	$AgCd_2$ or $AgCd_3$	

The specific volume method has been applied by Maey to the study of the potassium, sodium and lithium amalgams, but the numerous compounds formed in these series have led to the results being partly untrustworthy.

In the cadmium-arsenic alloys an example has been found of the existence of two compounds formed with expansion.

[1] *Zeit. phys. Chem.*, **38**, 292 (1901); **50**, 200 (1905).

In this case solid solutions do not occur, at least within wide limits: it was found that the curve consisted of two straight lines intersected by a third. Here, the points of intersection give the maxima of the compounds.

As a conclusion of these investigations we can affirm that the specific volumes of alloys which are simply mechanical mixtures can be calculated to within 1 per cent. by the mixture rule; deviations, when they occur are generally to be attributed to the formation of compounds.

C. Hoitsema [1] has made a contribution to the subject in a study of the density of the copper-gold and gold silver alloys. As is known, the density is the inverse of the specific volume. In the following table are shown some values for the copper-gold alloys; the calculated specific volumes have been obtained by the mixture rule and are concordant with those experimentally found.

COPPER-GOLD ALLOYS.

Gold, per cent.	Specific gravity at 15° C.	Specific volumes.		Difference.
		Observed.	Calculated.	
(100·0)	(19·26)	(·05192)	—	—
91·7	17·35	·05764	·05715	− ·9%
83·3	15·86	·06305	·06244	− 1·0 ,,
75·0	14·74	·06784	·06768	− ·3 ,,
58·3	12·69	·07880	·07820	− ·8 ,,
25·0	10·035	·09965	·09919	− ·5 ,,
0·0	(8·7)	(·11494)	—	—

Specific Heat of Intermetallic Compounds.

The energy content of solid bodies is a subject of great importance and is intimately bound up with that of crystal-

[1] *Zeit. anorg. Chem.*, **41**, 63 (1904).

line form. Domenico Guglielmini, in 1688 and 1705,[1] recognised that every substance has its own crystalline form, governed by definite rules. Among the many theories on the energy content of solid bodies is that of the uniform distribution of this energy. This has, however, recently been thrown in doubt by the investigations of Nernst and his co-workers on the relation between specific heat and temperature.

The kinetic theory of the energy content of a monatomic body, which is the simplest case, postulates that the function

$$\int_0^T C_v \, dT$$

is indicated by the oscillations of the atoms, which are supposed to be at rest at absolute zero. At a given temperature the atoms are in motion and, in an isotropic body, this motion occurs in three planes perpendicular to each other. With rise in temperature the energy content of bodies varies. For a solid body such energy is given by the displacement of the atoms from their equilibrium positions, or the localised potential energy.

According to Nernst,[2] considering the case in which atoms revolve in a circular path about their mean positions, and assuming that the force attracting them to such positions is proportional to the displacement,[3] the equation for the centrifugal force for an atom of mass m revolving with velocity u in a circle of radius r is

$$\frac{m}{r} u^2 = A \, r$$

where A is the force per unit displacement attracting the atom to its position of rest.

[1] On the works of this founder of crystallography see Guareschi: *Domenico Guglielmini e la sua opera scientifica.* Turin, 1914.

[2] *The Theory of the Solid State.* London, 1914, p. 11.

[3] Boltzmann: *Vorles u. Gastheorie,* II., 126.

The kinetic energy of the atom is

$$\frac{m}{2} u_1^2 = A \int r \, d r = A \frac{r^2}{r},$$

from which

$$\frac{m}{2} u^2 = \frac{m}{2} u_1^2,$$

which establishes the equality between kinetic and potential energy. Consequently, if it is known that the kinetic energy of a monatomic gas is $\frac{3}{2} RT = 2{\cdot}98T$ per gram atom, from the above equation the atomic heat of a monatomic solid body is

$$Cv = 3R = 5{\cdot}955,$$

for R = 1·985.

This simply expresses the law of Dulong and Petit.

For the content in heat energy of metallic compounds, as appears from two recent works of H. Schimpff [1] and F. Schubel,[2] the Neumann-Kopp law holds, according to which the molecular heat of a solid compound is equal to the sum of the molecular heats of the elements contained in it. The specific heat, c, of a compound is calculated from the equation

$$c = \frac{nM_1c_1 + mM_2c_2}{nM_1 + mM_2},$$

where c_1, c_2 are the specific heats, M_1, M_2 the atomic weights and n, m, the number of atoms of the components in the compound.

In metallic compounds, specific heat is an additive property. Before the study of metallic compounds had reached its present importance, Regnault [3] had shown that the specific heats of fusible metals followed the mixture rule at temperatures below the melting point, diverging therefrom at higher

[1] *Zeit. phys. Chem.*, **71**, 288 (1910).
[2] *Zeit. anorg. Chem.*, **87**, 101 (1914).
[3] *Ann. Ch. Phys.*, (3), **1**, 129 (1841).

temperatures. The recent investigations of Schübel show the additive character of the specific heats of metallic compounds.

The following table shows the results obtained by Schübel for a number of definite compounds at temperatures below their melting points.

Compounds.	Specific heats at						Melting Points.
	100°	200°	300°	400°	500°	600°	
Cu_2Mg	·1184	·1230	·1283	·1365	—	—	797°
Cu_3Al	·1093	·1135	·1167	·1205	·1260	—	1050°
CuAc	·1310	·1363	·1413	·1468	—	—	625°
$CuAl_2$	·1526	·1585	·1630	·1665	·1690	—	590°
Cu_3Sb	·0815	·0837	·0860	·0890	—	—	687°
Cu_2Sb	·0760	·0784	·0806	—	—	—	—
AgMg	·0910	·0942	·0974	·1004	·1042	·1070	820°
Ag_3Al	·0695	·0724	·0745	·0762	·0872	·0798	771°
Ag_2Al	·0763	·0785	·0806	·0831	·0868	·0913	721°
Ag_3Sb	·0560	·0574	·0630	—	—	—	559°
$MgZn_3$	·1180	·1234	·1292	·1450	—	—	595°
Ni_2Mg	·1305	·1385	·1424	·1460	·1480	·1508	1145°
Co_3Sn	·0824	·0876	·0900	·0926	·0944	·0962	—
Ni_3Sn	·0836	·0872	·0907	·0940	·0972	·1002	1162°
FeSi	·1465	·1540	·1600	·1645	·1690	·1720	—
NiSi	—	—	·1469	·1523	·1572	·1615	—
Ni_2Si	·1190	·1250	·1290	·1320	·1355	·1386	—
Mg_2Si	·2250	—	·2455	—	—	·2640	1102°

As a result of the preceding data it appears that the compounds Cu_2Mg, Cu_3Al, $CuAl_2$, AgMg, Ag_3Al, $MgZn_2$, Co_3Sn, follow the Neumann-Kopp law to within 2 per cent. Other compounds show greater deviations; the compound Ni_3Sn shows a deviation of about 7·3 per cent.

From the data given on p. 61 it appears that the Neumann-Kopp law is, especially for high temperatures, an approximate statement. The divergences between the observed and calculated values are independent of the temperature for nearly half the compounds shown. We shall refer to a

Molecular Heats of certain Metallic Compounds (Schübel).

Deviations of observed from calculated values.

	Mol. heats	— 150°	— 100°	0°	100°	200°	300°	400°	500°
Cu_2Mg	obs.	12·81	14·73	17·13	17·95	18·65	19·45	20·69	—
	calc.	12·88	14·89	17·37	18·11	18·68	19·29	19·78	—
	diff.	— 0·07	— 0·16	— 0·24	— 0·16	— 0·03	+ 0·16	+ 0·91	—
	%	— 0.06	— 1·1	— 1·4	— 0·9	— 0·2	+ 0·8	+ 4·6	—
Cu_3Al	obs.	16·28	19·08	22·60	23·82	24·73	25·43	26·26	27·46
	calc.	16·58	19·48	23·00	23·98	24·76	25·52	26·07	26·71
	diff.	— 0·30	— 0·40	— 0·40	— 0·16	— 0·03	— 0·9	+ 0·19	+ 0·75
	%	— 1·8	— 2·0	— 1·7	— 0·7	— 0·1	— 0·4	+ 0·7	+ 2·8
CuAl	obs.	7·58	9·10	11·10	11·88	12·36	12·82	13·32	—
	calc.	8.00	9·52	11·42	12·02	12.48	12·88	13·15	—
	diff.	— 0·42	— 0·42	— 0·32	— 0·14	— 0·12	— 0·06	+ 0·17	—
	%	— 5·2	— 4·4	— 2·8	— 1·1	— 1·0	— 0·5	+ 1·3	—
$CuAl_2$	obs.	11·70	14·07	17·04	17·98	18·67	19·20	19·61	19·22
	calc.	11·71	14·07	17·05	18·06	18·82	19·44	19·84	20·27
	diff.	— 0·01	0	— 0·01	— 0·08	— 0·15	— 0·2	—0·23	— 0.35
	%	— 0·1	0	— 0·1	— 0·4	— 0·8	— 1·2	—1·1	— 1·7
Cu_3Sb	obs.	19·44	21·60	24·28	25·33	26·01	26·73	27·66	—
	calc.	17·82	20·33	23·31	25·06	24·71	25·42	26·03	—
	diff.	+ 1·62	+ 1·27	+ 0·97	+ 1·27	+ 1·30	+ 1·31	+ 1·63	—
	%	+ 9·0	+ 6·2	+ 4·1	+ 5·2	+ 5·2	+ 5·1	+ 6·2	—
Cu_2Sb	obs.	14·40	15·99	17·97	18·79	19·32	19·94	—	—
	calc.	13·53	15·35	17·52	18·08	18·57	19·10	—	—
	diff.	+ 0·87	+ 0·64	+ 0·45	+ 0·71	+ 0·75	+ 0·84	—	—
	%	+ 6·4	+ 4·1	+ 2·6	+ 3·9	+ 4·0	+ 4·4	—	—
AgMg	obs.	8·76	9·90	11·36	12·02	12·46	12·88	13·26	13·79
	calc.	9·27	10·39	11·80	12·23	12·54	12·91	13·26	13·81
	diff.	— 0·51	— 0·49	— 0·44	— 0·21	— 0·08	— 0·03	0	— 0·02
	%	— 5·5	— 4·7	— 3·7	— 1·7	— 0·6	— 0·2	0	— 0·2
Ag_3Al	obs.	19·08	20·92	23·36	24·56	25·40	26·14	26·73	27·43
	calc.	18·62	20·92	23·66	24·28	24·76	25·31	25·89	27·16
	diff.	+ 0·46	0	— 0·30	+ 0·28	+ 0·64	+ 0·83	+ 0·84	+ 0·27
	%	+ 2·5	0	— 1·3	+ 1·2	+ 2·6	+ 3·0	+ 3·2	+ 1·
Ag_2Al	obs.	13·77	15·45	17·70	18·53	19·07	19·58	20·18	21·08
	calc.	13·65	15·46	17·65	18·20	18·62	19·06	19·49	20·38
	diff.	+ 0·12	— 0·01	+ 0·05	+ 0·33	+ 0·45	+ 0·52	+ 0·69	+ 0·70
	%	+ 0·9	0	+ 0·3	+ 1·8	+ 2·4	+ 2·7	+ 3·5	+ 3·5
Ag_3Sb	obs.	20·48	22·44	24·52	24·85	25·47	27·95	—	—
	calc.	19·86	21·67	23·97	24·36	24·71	25·21	—	—
	diff.	+ 0·62	+ 0·77	+ 0·55	+ 0·49	+ 0·76	+ 2·74	—	—
	%	+ 3·1	+ 3·5	+ 2·3	+ 2·0	+ 3·1	+ 10·8	—	—
$MgZn_2$	obs.	13·71	15·27	17·37	18·31	19·15	20·05	—	—
	calc.	13·98	15·57	17·71	18·69	19·44	20·05	—	—
	diff.	— 0·27	— 0·30	— 0·34	— 0·38	— 0·29	0	—	—
	%	— 1·9	— 1·9	— 1·9	— 2·0	— 1·5	0	—	—
Ni_2Mg	obs.	—	14·18	16·80	18·50	19·64	20·19	20·70	20·99
	calc.	—	14·51	17·91	19·45	20·92	22·05	21·46	21·77
	diff.	—	— 0·33	— 1·11	— 0·95	— 1·28	— 1·86	— 0·76	— 0·78
		—	— 2	— 6·3	— 4·9	— 6·1	— 8·4	— 3·5	— 3·6

rational interpretation of the divergences shown with rise in temperature in the following pages.

ATOMIC HEATS OF CERTAIN METALLIC COMPOUNDS

(FROM SCHÜBEL.)

Compounds	100°	200°	300°	400°	500°	600°
Cu_2Mg	5·98	6·22	6·48	6·89	—	—
Cu_3Al	5·95	6·18	6·36	6·56	6·86	—
CuAl	5·94	6·18	6·41	6·66	—	—
$CuAl_2$	5·99	6·22	6·40	6·54	6·64	—
Cu_3Sb	6·33	6·50	6·68	6·91	—	—
Cu_2Sb	6·26	6·44	6·65	—	—	—
AgMg	5·89	6·23	6·44	6·63	6·89	7·07
Ag_3Al	6·14	6·35	6·54	6·68	6·86	7·00
Ag_2Al	6·17	6·36	6·53	6·73	7·03	7·40
Ag_3Sb	6·21	6·37	6·99	—	—	—
$MgZn_2$	6·10	6·38	6·68	7·48	—	—
Ni_2Mg	6·17	6·55	6·73	6·90	6·98	7·12
Co_2Sn	6·51	6·92	7·10	7·33	7·46	7·60
Ni_3Sn	6·17	6·48	6·70	6·95	7·18	7·39
FeSi	6·16	6·48	6·74	6·93	7·11	7·25
NiSi	5·73	—	6·39	6·64	6·85	7·04
Ni_2Si	5·77	6·07	6·27	6·40	6·59	7·67
Mg_2Si	5·78		6·31	—	—	6·79

The relation of atomic heat to temperature above 100° is generally almost linear. If the above values are plotted along with the known values for the pure metals it will be seen that the behaviour of intermetallic compounds is perfectly similar to that of pure metals.

Inasmuch as the figures quoted do not show a perfect concordance between observed and calculated values, the Neumann-Kopp law must be considered as an approximation, particularly at high temperatures.

Planck's [1] *quantum* theory, proposed in his researches on the phenomena of radiation has been generalised by

[1] *Theorie d. Wärmestrahlung*, p. 157. Leipzig, 1906.

Einstein [1] for the movements of atoms; it gives a rational explanation of the deviations from the law of Dulong and Petit, which forms the foundation for that of Neumann-Kopp.

Einstein's formula for the total energy content W of a gram atom is given by the equation, deduced from the ordinary equations for the distribution of energy,

$$W = 3\,R\frac{\beta\gamma}{e^{\frac{\beta\nu}{T}}-1},$$

and for atomic heat, differentiating with respect to T:—

$$\frac{d\,W}{d\,T} = 3\,R\frac{e^{\frac{\beta\nu}{T}}\left(\frac{\beta\,\nu}{T}\right)^2}{\left(e^{\frac{\beta\,\nu}{T}}-1\right)}.$$

According to the *quantum* theory, definite limits are assigned to the oscillations of an atom about its equilibrium position. In the case of a solid monatomic body it may be assumed that its molecules are surrounded by a gas which may be considered monatomic for simplicity. The molecules of this gas oppose the oscillations of the atoms of the solid body, producing thereby a condition of equilibrium. For a monatomic gas the number of oscillations is nil; it can move freely by its kinetic energy according to Maxwell's conception. But for a solid body or any other union of molecules the *quantum* theory leads to other results. Einstein's formula, which gives the specific heat as a function of the temperature, leads to a simple qualitative result. Quantitatively there are divergences between theory and observation which increase at low temperatures.

Nernst and Lindemann [2] have amended the formula of Einstein, introducing in addition to the number of oscillations r a second number $\frac{\nu}{2}$ which gives values more in

[1] *Ann. d. Phys.*, **22**, 180 (1907).
[2] *Ber.*, **43**, 26 (1910).

accordance with experiment. The Nernst-Lindemann formula is the following :—

$$C_\nu = \frac{dW}{dT} = \frac{3}{2}R\left[\frac{\frac{\beta\nu}{eT}\left(\frac{\beta\nu}{T}\right)^2}{\left(\frac{\beta\nu}{eT}-1\right)^2}\cdot\frac{\frac{\beta\nu}{e\,2T}\left(\frac{\beta\nu}{2T}\right)^2}{\left(\frac{\beta\nu}{e\,2T}-1\right)^2}\right]$$

Although it has been shown necessary to introduce into Einstein's formula a greater number of oscillations, the value $\frac{\nu}{2}$ in the above formula has no theoretical basis.

Other theoretical possibilities with regard to the relation of specific heat and temperature have been discussed by Debye [1] and Duclaux.[2] We must, however, limit our treatment of the subject to the short outline given above.

Electrical Conductivity.

The problem of the electrical conductivity of alloys has become of considerable importance with the development of modern metallography—an importance both theoretical and practical because alloys with constant and small temperature coefficients are of great use in electrotechny. The first exhaustive study of this subject was made by Matthiessen.[3] In his earlier researches Matthiessen found that binary mixtures of metals can be divided into two groups ; in the first the conductivity, σ, is an additive property as in the case of alloys of lead zinc, tin and cadmium ; in the second group the conductivity is less than that calculated by the mixture rule, as in the case of alloys of copper, silver, gold, aluminium, bismuth, platinum, antimony, iron and others. These two types of conductivity curves are shown in Fig. 19. The abscissæ represent the percentage of the second component and the ordinates the con-

[1] *Ann. d. Phys.*, **39**, 789 (1912).
[2] *C. R.*, **155**, 1015, 1509 (1912).
[3] *Pogg. Ann.*, **103**, 428 (1858) ; **110**, 190 (1860) ; **116**, 369 (1862) ; **122**, 19 and 68 (1864).

ductivity. The straight line I. indicates that in a mixture of two metals the conductivity can be calculated by the mixture rule, *i.e.*, the conductivity of the alloy is the sum of the single conductivities of its constituents obtained from their relative proportions. Curve II. shows the course of conductivity in alloys of the second group.

If a quantity of an element of the second group be added to a metal of the first group the conductivity curve will be

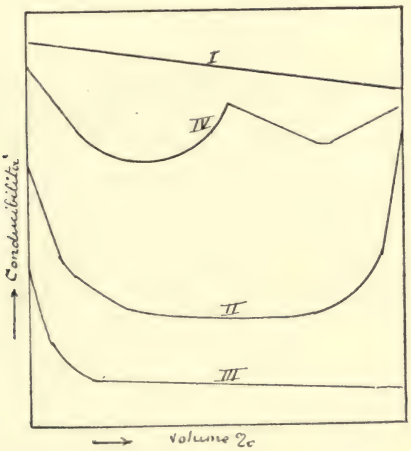

FIG. 19.

lowered appreciably and the curve will be of the type III. Curve IV. represents the case of the formation of a compound.

Among the investigations carried out on the conductivity of metallic alloys must also be mentioned those of Le Chatelier [1] and Liebenoff.[2] Lord Rayleigh [3] has also discussed the matter on the theoretical side.

[1] *C. R.*, **112**, 40 (1891); **126**, 1709 (1898).
[2] *Zeit. Elektr.*, **4**, 201 (1897—98).
[3] *Nature*, **54**, 154 (1896).

Le Chatelier attempted to give an explanation of the diverse behaviour of the metals of Matthiessen's first and second groups. If an alloy is a " mixture of crystals " of two metals, the conductivity may be calculated by the mixture rule ; but if it forms " crystals of mixture " the values of the conductivity are then different.[1] Le Chatelier further noted that the addition of small quantities of non-metals, such as phosphorus, carbon and arsenic, exercised a great influence on the conductivity of certain metals. The conductivity of iron, for example, is greatly altered by the addition of small quantities of carbon.[2]

The electrical conductivity method has been used of late years to define the existence of various intermetallic compounds. By the investigations of Guertler,[3] of Kurnakoff and Zemczuzny [4] and of Stepanoff,[5] it has become one of the most valued methods of investigation for the solution of problems left unsolved by the thermal method. The experimental methods followed in the investigations mentioned are based on measurements of conductivity or of specific resistance.

Matthiessen's Rule.

If the relative increase of conductivity between 0° and 100° be expressed by the equation—

$$P(\sigma) = 100\,\frac{\sigma_0 - \sigma_{100}}{\sigma_0} = 100\,\frac{\varrho_{100} - \varrho_0}{\varrho_{10}},$$

where σ_0, σ_{100} are the conductivities at 0° and 100° respectively, and ϱ_0, ϱ_{100}, the specific resistances, then for pure metals $P(\sigma) = 29$.

If σ_m and $P_m(\sigma)$ are the numerical values calculated by

[1] *Cf.* Chiwolson. *Traite de Phys.*, IV., 1003 (1910).
[2] *Cf.* Benedicks : *Zeit. phys. Chem.*, **40**, 545 (1902).
[3] *Zeit. anorg. Chem.*, **51**, 397 (1906), **54**, 58 (1907).
[4] *Ibid.*, **54**, 149 (1907) ; **60**, 1 (1908).
[5] *Ibid.*, **60**, 209 (1908) ; **78**, 1 (1912).

the mixture rule Matthiessen's rule is expressed by the following equation :—

$$\frac{\sigma}{\sigma_m} = \frac{P(\sigma)}{P_m(\sigma)}.$$

The value of $P_m(\sigma)$ is about 29.

Barus' Rule.

Barus,[1] from the expression

$$P(\sigma) = 100\,\frac{\varrho_{100} - \varrho_0}{\varrho_0} = 100\,\frac{\sigma_0 - \sigma_{100}}{\sigma_{100}},$$

obtained for pure metals $P(\sigma) = 41$.

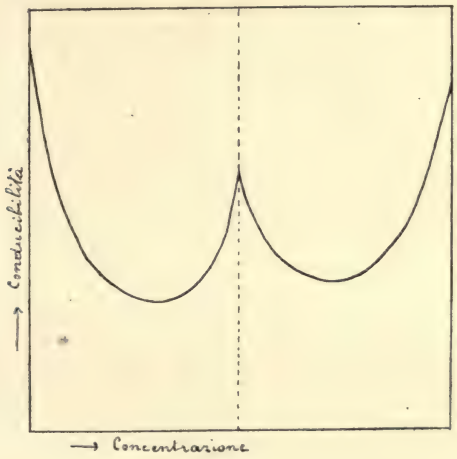

Fig. 20.

This equation has since been discussed and amended by Guertler who has adapted it to many experimental divergences ; it retains, however, its empirical character.

We pass on to state certain general relations established by Guertler in his interesting investigations. With regard

[1] *Amer. Journ. of Sci.*, (3), **36**, 427 (1888).

to the nature of conductivity diagrams the following rule holds :—

When, in a series of alloys between two metals m compounds are formed, the diagram consists of $m + 1$ binary systems.

Generally, compounds have a conductivity less than that of their most conductive component.[1] When a compound forms solid solutions with both components the diagram showing relation between conductivity and composition assumes the form of Fig. 20.

The conductivity method has been of great help in the study of equilibrium diagrams, especially in cases where compounds are formed. In the following table are shown some systems studied both thermally and by the method of electrical conductivity. The results, as will be seen, are very concordant :—

System.	Formulæ of compounds deduced.	
	By thermal method.	By electrical conductivity method.
Au — Sn	$AuSn$	$AuSn$
	$AuSn_2$	$AuSn_2$
	$AuSn_4$	$AuSn_4$
Au — Pb	$AuPb_2$	$AuPb_2$
Cu — Sn	Cu_4Sn	Cu_4Sn
	Cu_3Sn	Cu_3Sn
	$CuSn$	$CuSn$
Cu — Sb	Cu_2Sb	Cu_2Sb
	Cu_3Sb	Cu_3Sb
Sb — Sn	$SbSn$	$SbSn$

Apart from the direct measure of conductivity or specific resistance of intermetallic compounds, a factor which is of great importance and which has entered into common use

[1] A rule noted by Matthiessen in his investigations already recorded.

is the temperature coefficient of conductivity. This coefficient has been determined for many intermetallic compounds. Some values are shown in the following Table :—

Alloys.	Compounds.	Temperature coefficients of resistance.
Mg — Pb	Mg_2Pb	·00250
Mg — Sn	Mg_2Sn	·00445
Mg — Cu	$MgCu_2$	·00316
	Mg_2Cu	·00365
Mg — Zn	$MgZn_2$	·00290
Mg — Bi	Mg_3Bi_2	·00370
Mg — Ag	MgAg	·00310
	$MgAg_3$	·00309
Mg — Cd	MgCd	·00417
Sn — Sb	Sn_3Sb_2	·00361
	SnSb	·00343
Cu — Sn	Cu_3Sn	·00350
	CuSn	·00300
Cu — Zn	CuZn	·00360
	$CuZn_2$	·00408
	$CuZn_6$	·00355
Cu — As	Cu_3As	·00250

Like many other physical constants, the temperature coefficient of conductivity is a characteristic function of the composition of an alloy. The observations made on p. 64 on conductivity curves hold also for this constant.

Alloys which have a small temperature coefficient are very important from the technical point of view ; they are generally used in the construction of resistance cells. Such alloys do not, however, correspond to any definite compounds but are really solid solutions. Where solid solutions are formed between two metals, the curve passes through a minimum and so the alloys used in practice correspond pretty closely in composition to that indicated by such minimum.

Magnetic Properties

The magnetic properties of alloys have been used in some cases to throw additional light on the formation of compounds; but the information which we possess on this branch of the subject does not permit the establishment of any general rules. Up to the present, the chief studies have been made on those alloys which have some practical importance.

The most important work on metallic compounds is that of Tammann,[1] but before discussing his results in detail, it will be well to summarise the fundamental principles of the magnetic properties of metals.

Although, according to Faraday,[2] magnetic bodies can be classed as paramagnetic or diamagnetic, it may be more useful to follow the classification of Chwolson [3] who divides substances into two groups: (1) the ferromagnetic or strongly magnetic substances such as iron, steel, nickel, cobalt and certain alloys; and (2) weakly magnetic substances; this group includes both paramagnetic and diamagnetic bodies.

In alloys, magnetic properties vary according to the nature of the constituents. It is most particularly of interest to follow the variations where ferromagnetic bodies are in alloy with substances of different magnetic nature.

Tammann has given two rules which have an almost general validity:—

I. *Binary combinations of ferromagnetic metals with other metals are nearly always non-magnetic or only slightly magnetic.*

This rule has been deduced from the study of the magnetic properties of alloys of iron, cobalt and nickel with silicon, tin, aluminium, antimony, bismuth, magnesium and zinc. In this series of alloys the following compounds occur:—

[1] *Zeit. phys. Chem.*, **65**, 73 (1909).
[2] *Phil. Trans.*, **136**, (1846); *Pogg. Ann.* **68**, 105 (1846).
[3] *Traité de Phys.*, IV., 830, 884 (1910).

Fe.	Co.	Ni.
FeSi	Co_2Si, Co_3Si_2, CoSi, $CoSi_2$, $CoSi_3$	Ni_3Si, Ni_2Si, Ni_3Si_2, NiSi, $NiSi_3$
$Fe_x Sn_y$	Co_2Sn, CoSn	Ni_3Sn_2, Ni_3Sn, Ni_4Sn (?)
$FeAl_3$	CoAl, Co_2Al_5, Co_3Al_{13}	$NiAl_3$, $NiAl_2$, NiAl
$FeSb_2$ Fe_3Sb_2	CoSb, $CoSb_2$	Ni_4Sb_5, NiSb, Ni_5Sb_2, Ni_4Sb
—	—	NiBi, $NiBi_3$
—	—	Ni_2Mg, $NiMg_2$
$FeZn_7$, $FeZn_3$	$CoZn_4$	$NiZn_3$

K. Honda [1] in a further study of the alloys nickel-chromium, nickel-tin, nickel-aluminium, cobalt-chromium and iron-vanadium has confirmed this rule of Tammann. A. Friedrich [2] has found that it only holds for binary combinations of ferromagnetic metals with other elements of a purely metallic character; the compounds formed with elements of a metalloidal character are magnetic. Such, for example, are the following compounds :—

$$Co_5As_2,\ Fe_3P,\ Fe_2P,\ Fe_2S.$$

The borides of iron, cobalt and nickel are magnetic, although not to a high degree, as Moissan [3] has observed.

II. *Alloys consisting of mixed crystals in which a ferromagnetic metal preponderates are magnetic; those in which the ferromagnetic metal does not act as solvent* (i.e., *is present in relatively small amount*) *are non-magnetic.*

This rule also has been confirmed by Honda. An instance of it is given by the amalgams of the three ferromagnetic elements. Nagaoka [4] found that the amalgams of iron and cobalt are strongly magnetic, while the nickel amalgams as H. Wünsche [5] has observed, are only slightly magnetic.

A systematic study is desirable of magnetic properties in

[1] *Ann. d. Phys.*, (4), **32**, 1003 (1910).
[2] *Metall.*, **3**, 129 (1908); **5**, 593 (1908).
[3] *C. R.*, **120**, 173 (1895); **122**, 424 (1896).
[4] *Wied. Ann.*, **59**, 66 (1896); *Zeit. phys. Chem.*, **22**, 641 (1897).
[5] *Ann. d. Phys.*, (4), **7**, 116 (1902).

relation to chemical composition ; the subject is somewhat obscure by reason of the numerous anomalies encountered in practice which have to be explained by particular reservations contrary to the spirit of general principles.

An interesting phenomenon which has recently been used in the theoretical treatment of the metallic properties of metals is presented by ferromagnetic alloys composed of non-magnetic metals.

Hogg,[1] in 1892, had observed that while certain ferromanganese alloys are non-magnetic, they acquire by the addition of aluminium approximately the same magnetic properties as iron. Heusler [2] subsequently noticed the same phenomenon in the manganese-copper alloys, which are non-magnetic but become magnetic by addition of aluminium, tin, bismuth, antimony, arsenic or boron. The most strongly magnetic alloys, however, are those obtained by addition of aluminium in the exact proportions required for the two compounds Mn_3Al and Cu_3Al.

Heusler has, therefore, suggested that the ferromagnetism of such alloys is only to be sought in the chemical compounds resulting among the constituent metals. These combinations would have the following formula :—

$$Al_xMn_yCu_{3x-y}.$$

The ferromagnetism of these compounds has been discussed by Richarz, a pupil of Heusler, from the point of view of the electron theory ; he supposes that electrons have a greater degree of mobility in compounds than in pure metals. This supposition, though not well established, fits in with J. J. Thomson's theory, according to which the electrical conductivity of metals is due to a transport of electrons.[3]

E. Wedekind,[4] in a study of the magnetisation of mag-

[1] *Chem. News.*, **66**, 140 (1892).

[2] *Zeit. angew. Chem.*, **17**, 260 (1904) ; Richarz and Heusler, *Zeit. anorg. Chem.*, **61**, 265 (1909) ; **65**, 110 (1910).

[3] *Cf. The Corpuscular Theory of Matter*, p. 49. London, 1907.

[4] *Zeit. phys. Chem.*, **66**, 614 (1909).

netic compounds composed of non-magnetic elements, has also recognised that ferro-magnetism is not only an atomic property as in the case of iron, nickel and cobalt, but may also be a molecular property. It may further be mentioned that the elements which are magnetic either in alloys or compounds are found in a definite region of the Periodic System, *i.e.*, at the end of the fourth horizontal series ; they are elements whose atomic weights lie between 52·1 and 59, chromium, manganese, iron, nickel and cobalt.

Electrolytic Potential.

Electrolytic potential in the same way as the other physical properties hitherto considered is a function of composition ; a knowledge of this quantity is often of great value in the investigation of metallic alloys. It is, further, of practical importance in so far as it bears on the corrosion of alloys in electrolytic liquids. We shall allude briefly to the principal deductions made in this branch of research. The actual knowledge which we have of the conditions of equilibrium between an electrolyte and an alloy containing a chemical compound capable of forming solid solutions is somewhat scanty.

The most valuable investigations on electrolytic potential are those of W. Reinders [1] and N. Pushin.[2] The theoretical ideas which have been used in these studies are based on the concept of electrolytic solution pressure introduced into physical chemistry by Nernst [3] in 1889.

When a metal is immersed in a solution of one of its salts a difference of potential is set up between metal and solution ; from this difference of potential originates electromotive force.

Theoretically, however, the problem is more complicated than it appears at first sight. In fact, in the interpretation

[1] *Zeit. phys. Chem.*, **42**, 225 (1903).
[2] *Zeit. anorg. Chem.*, **56**, 1 (1908) ; **62**, 34 (1909).
[3] *Zeit. phys. Chem.*, **4**, 150 (1889).

of the case above mentioned it is necessary to take account of the opposition of the ions of the salt which tends to neutralise the solution pressure of the metal; this opposing force is, of course, the osmotic pressure of the ions of the electrolyte.[1]

Laurie[2] and M. Herschkovitch[3] studied different alloys immersed in a solution of a salt of one of the component metals. They noticed in the curves for electro-motive force a number of discontinuities, particularly in the alloys copper-tin and gold-tin, where the discontinuities corresponded to the compounds Cu_3Sn and AuSn respectively. In these studies, however, Laurie did not take into account the concentration of the electrolyte, a factor of fundamental importance if reliable generalisations are to be made.

Herschkovitch used a normal solution of a salt of the more positive metal. He draws attention to the principles of the phase rule and shows how they can elucidate the variations of potential in alloys. These variations can be grouped in the following four cases :—

I. *The two metals separate in a pure state from their solutions.*

II. *The metals are soluble in the solid state to a limited degree.*

In this case Gibbs' principle may be applied, namely, that "the potential of all the components in the total of the system is constant."

III. *The metals are completely soluble. The potential varies continuously with the composition.*

IV. *In the solidification of fused mixtures of the metals a new phase (compound) is formed. For n compounds there will be "n" discontinuities on the potential curve.*

Herschkovitch, from studies of the form of potential

[1] *Cf.* "*Elettrochimica,*" G. Carrara, in "*Nuova Enciel. di Chimica,*" I. Guareschi, p. 494, Vol. I. (1906).

[2] *J. C. S.*, **53**, 104 (1888); **55**, 677 (1889); **65**, 1031 (1894). *Phil. Mag.* (5), **33**, 94 (1892).

[3] *Zeit. phys. Chem.*, **27**, 123 (1899).

curves, deduced the formation of the following binary compounds :—

$ZnSb_2$, Zn_4Ag, Zn_2Cu, $SnAg_4$ and $SnCu_3$.

Reinders' Classification.—Reinders' work, already mentioned, is the most important theoretical contribution to our knowledge of the variations of electrolytic potential among metallic alloys. We shall describe briefly the different cases that can arise in alloys constituted of simple conglomerates or solid solutions. More particular attention will be given to the case in which a compound occurs.

I. *The two metals form solutions from which the components separate in the pure state.* Let M_1, M_2 be the two metals and M_1Z, M_2Z, the corresponding salts. The electrolyte is assumed to be a homogeneous-phase. The difference of potential between the pure metal M_1 and the electrolyte containing M_1Z, is calculated from Nernst's [1] formula :—

$$x_1 = \frac{R\,T}{n_1 F} \log \frac{P_1}{p_1},$$

where P_1 is the electrolytic solution pressure, p_1 the osmotic pressure of the cations M_1, n_1 the valency of M_1, $\frac{R}{F}$ the electrolytic constant of gases and T the absolute temperature.

When part of the ions of M_1 are substituted by ions of M_2, p_1 becomes smaller and hence x_1 becomes greater. The same argument applies to x_2 ; the difference of potential between the metal M_2 and a solution of M_2Z is influenced by the presence of ions of M_1 as in the first case. For equilibrium

$$x_1 = x_2.$$

Representing graphically the values x_1, x_2 as a function of the composition of an electrolyte in which the total concentration of the ions is constant, the curve shown in Fig. 21 is obtained. A point in the line $A\ D$ gives the difference of potential and the concentration of the electrolyte in equili-

[1] *Zeit. phys. Chem.*, **22**, 539 (1898).

brium with the metal M_1; similarly a point in $B\,D$ gives the difference of potential and the concentration of the electrolyte in equilibrium with the metal M_2. At the point D the electrolyte is in equilibrium with both metals. For this point $x_1 = x_2$, or

$$\frac{1}{n_1} \log \frac{P_1}{p_1} = \frac{1}{n_2} \log \frac{P_2}{p_2},$$

or

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}$$

and putting $n_1 = n_2$

$$P_1 : P_2 = p_1 : p_2.$$

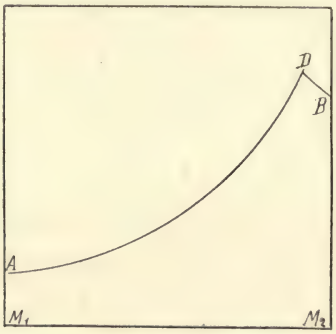

FIG. 21.

The ratio of the ionic concentrations in the equilibrium condition is equal to the ratio of the electrolytic solution pressures.

II. *The two metals form mixed crystals with each other.* In this case the electrolytic solution pressure of M_1 is lowered by presence of M_2; when in the metallic phase there are x atoms of M_2 and $1-x$ atoms of M_1 (x being very small), the lowering of the solution pressure is proportional to the number of molecules of the second metal which are in the solution. The solution pressure of the first metal is

P' $(1-x)$ and of the second Kx, in which K is an unknown factor. For equilibrium—

$$\sqrt[n_1]{\frac{P'\,(1-x)}{p_1}} = \sqrt[n_2]{\frac{Kx}{p_2}},$$

or

$$\frac{\sqrt[n_2]{p_2}}{\sqrt[n_1]{p_1}} = \frac{\sqrt[n_2]{Kx}}{\sqrt[n_1]{P'\,(1-x)}},$$

and if $n_1 = n_2$

$$\frac{p_2}{p_1} = \frac{K}{P'} \cdot \frac{x}{1-x};$$

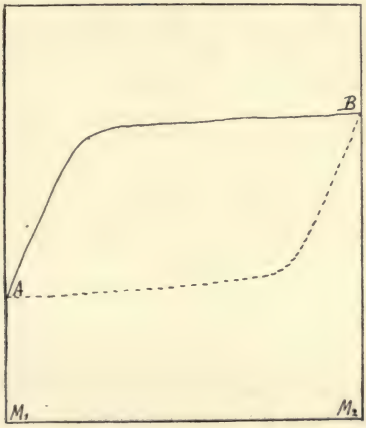

FIG. 22.

which means that the ratio of the ions in the electrolyte is, in atomic proportions of the metals, as $K : P'$. If the two metals form a continuous series of mixed crystals the potential curve assumes the form of Fig. 22, in which the continuous line represents the metallic phase and the dotted line the corresponding electrolyte. When there is a gap in the series of mixed crystals the two cases represented in Figs. 23 and 24 are exemplified. The two components form

two series of solid solutions ; between the limits C and D the two metallic phases are in equilibrium. At E the electrolyte co-exists. The type represented by Fig. 23 has been found by Herschkovitch [1] in the cadmium-tin and cadmium-lead alloys. The type shown in Fig. 24 has been met with by the same author in the zinc-tin and zinc-lead alloys and also by Jaeger [2] and Bijl [3] in the cadmium amalgams.

III. *The two metals form a compound.* If the compound forms ions of its own composition the curve shows a maxi-

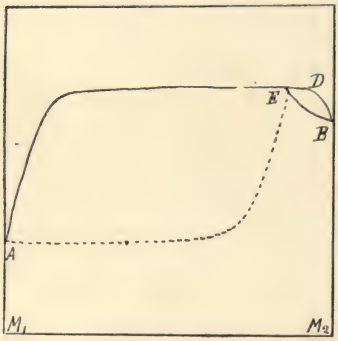

FIG. 23.

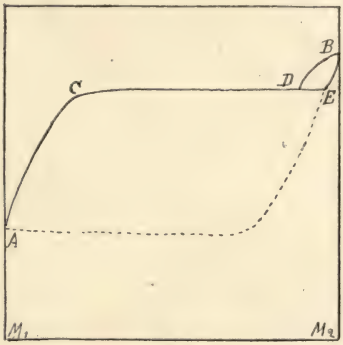

FIG. 24.

mum as in Fig. 25. The solution tension of the compound, as in the case of a pure metal, is a specific constant. Indicating it by $P_{1\cdot 2}$ we obtain by Nernst's formula—

$$x = \frac{R\,T}{n_{1\cdot 2}\,F} \log \frac{P_{1\cdot 2}}{p_{1\cdot 2}}.$$

The ions of the compound are dissociated into the ions of the components, and if in the component there are a atoms of M_1 and b atoms of M_2, equilibrium will exist when

$$p_1{}^a\, p_2{}^b = K\, p_{1\cdot 2}.$$

If the total concentration of the ions $p_1 + p_2$ is constant,

[1] *Loc. cit.*
[2] *Wied. Ann.*, **65**, 106 (1898).
[3] *Zeit. phys. Chem.*, **41**, 641 (1902).

$p_{1\cdot 2}$ reaches a maximum when $p_1 : p_2 = a : b$. In other words *x reaches a maximum*[1] *when the ratio of the ions* M_1 *and* M_2 *in the electrolyte is equal to the ratio of the metals in the compound.* This case is indicated in Fig. 25. Along AG the potential is that of the electrolyte in equilibrium with pure M_1; G is a non-variant point in which the electrolyte of that composition is in equilibrium with M_1 and the compound M_1M_2. The solid phase in equilibrium with electrolytes lying between G and K is the compound

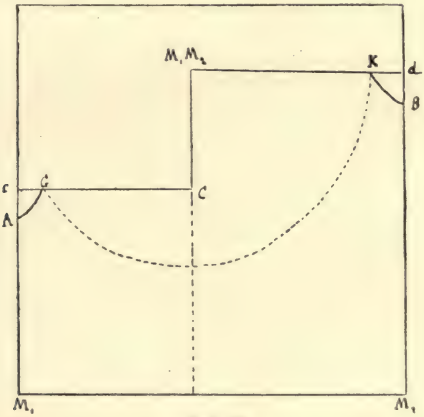

FIG. 25.

M_1M_2, and the potential follows the dotted curve. K is another non-variant point in which the compound M_1M_2 and the pure component M_2 co-exist with the electrolyte. Along KB the electrolyte is in equilibrium with component M_2.

If n compounds are formed between the two metals M_1 and M_2, for the point corresponding to each compound there occurs in the curve a fall of potential, so that there are n falls of potential as Herschkovitch stated.

Reinders discusses also the cases in which the compound forms series of mixed crystals with the components M_1 and

[1] Thus in Reinders' paper. It would appear, however, that when $p_{1\cdot 2}$ is a *maximum*, x should be a *minimum*.—TRANSLATOR'S NOTE.

M_2. From what has been said already, however, the form of the potential curve will be quite clear in this as in the other cases, since the diagram is a combination of the types comprised in it.

The complications which may occur in potential curves when, in addition to a compound, other variable phases appear with more or less wide limits, render the method somewhat unreliable, so that it is not always possible from observations of potential to deduce the true composition of the compound.

A. Sucheni,[1] in a study of the potential of thallium amalgams, noted that the compound Hg_2Tl formed solid solutions with mercury at an atomic concentration of 33·3 per cent. of thallium. The electromotive force increases up to the concentration of the compound, after which it remains constant. L. Cambi [2] has recently used the measurements of electrolytic potential to corroborate the equilibrium diagrams of the calcium and magnesium amalgams made from thermal data (see Chapter V).

In the following table are shown some results obtained by Pushin in the study of the electrolytic potential of various binary alloys in which definite compounds exist. These results are not always in accord with those obtained by the thermal method.

System.	Compounds found by Pushin.	Compounds now admitted.
Ag-Se	Ag_2Se	Ag_2Se
Ag-Te	Ag_2Te	Ag_2Te, AgTe
Cu-Te	CuTe, Cu_2Te	Cu_4Te, Cu_2Te
Pb-Te	PbTe	PbTe
Sn-Te	SnTe	SnTe
Sn-Cu	$SnCu_2$, $SnCu_3$	$SnCu_2$
Sn-Ag	$SnAg_3$, Ag_6Sn or Ag_5Sn	$SnAg_3$
Sn-Au	Sn_2Au, SnAu	SnAu, Sn_2Au, Sn_4Au
Zn-Cu	Zn_8Cu, Zn_2Cu, ZnCu, $ZnCu_2$	ZnCu, Zn_3Cu_2
Zn-Ag	Zn_6Ag, Zn_4Ag, Zn_2Ag, ZnAg	Zn_2Ag_3, ZnAg, Zn_3Ag_2, Zn_5Ag_2
Zn-Au	Zn_3Au ?, Zn_2Au, ZnAu	ZnAu, Zn_5Au_3, Zn_2Au
Cd-Cu	Cd_2Cu	$CdCu_2$, Cd_3Cu_2

[1] *Zeit. f. Elektroch*, **12**, 726 (1906).
[2] *R. Acc. Lincei*, **23**, II. (1914); **24**, I. (1915).

Thermo-electric Power.

The study of the variation of thermo-electric power with the composition of an alloy has only recently been made in a systematic way by E. Rudolfi [1] and W. Haken.[2] The researches of E. Becquerel [3] had led to the belief that the thermo-electric power of an alloy reaches its maximum when the components are present in equivalent proportions. The recent studies have shown this generalisation to be incomplete, but the fact noted by Becquerel served to call attention to this important field of study.

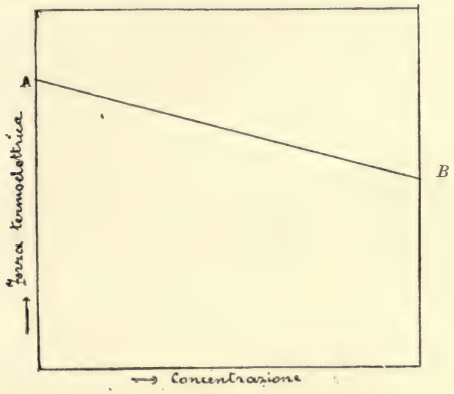

FIG. 26.

It is known that in a "couple" of two metals the magnitude of the electromotive force E depends on the temperature as well as the nature of the metals. In addition to the researches of Becquerel on the measure of E in alloys, the earlier work of Siebeck [4] and C. L. Weber [5] should be mentioned.

[1] *Zeit. anorg. Chem.*, **67**, 65 (1910).
[2] *Ann. d. Phys.*, (4), **32**, 291 (1910).
[3] *Ann. Chim. Phys.*, (4), **8**, 408 (1866).
[4] *Gilb. Ann.*, **73**, 115, 480 (1823); *Ann. Chim. Phys.*, 199 (1823).
[5] *Wied. Ann.*, **23**, 447 (1884).

Rudolfi studied the thermo-electric power of various alloys, as—

1. Tin-cadmium.
2. Tin-zinc.
3. Cadmium-zinc.
4. Tin-lead.
5. Bismuth-cadmium.
6. Lead-antimony.
7. Gold-silver.
8. Gold-copper.
9. Nickel-copper.
10. Platinum-palladium.

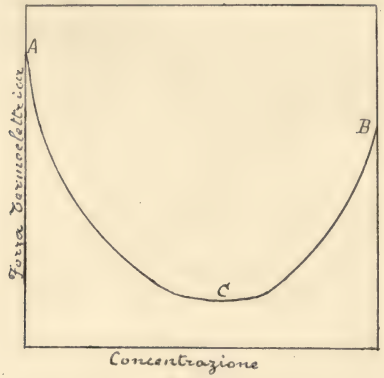

FIG. 27.

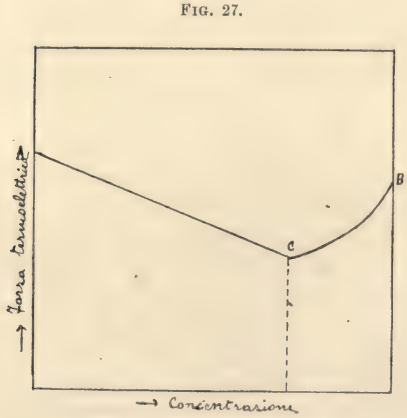

FIG. 28

He gives a general summary of the variations of thermo-electric power with the composition of alloys, laying down the following four types with accompanying diagrams.

TYPE 1. *The two components mix in the liquid state but solidify separately.*—The curve of thermo-electric power assumes the form indicated in Fig. 26. It is a continuous line which can be calculated by the mixture rule.

TYPE 2. *The two components form a series of mixed crystals.*—The curve here assumes the form of Fig. 27, showing a continuous variation passing through a minimum.

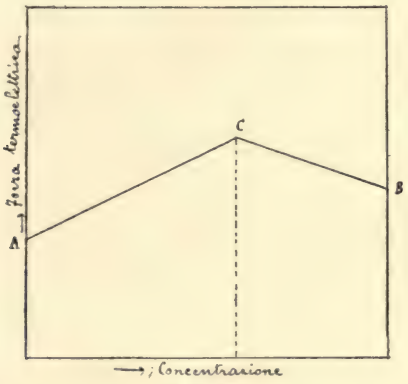

FIG. 29.

TYPE 3. *The two components form a limited series of mixed crystals.*—The curve (Fig. 28) shows that along *B C* mixed crystals separate while along *A C* conglomerates of mixed crystals together with the pure component separate.

TYPE 4. *The two components form a compound.*—The point *C* of Fig. 29 shows the composition of the compound. If solid solutions are formed in addition to the compound, the curve is modified according to cases 2 and 3, but this aspect of the problem is not yet well worked out. Haken (*loc. cit.*), who has studied the alloys of tellurium with antimony, tin, bismuth and lead, has succeeded in determining the limits of

chemical combination in these alloys. He has further noted that for an alloy which shows a smaller electrical conductivity the thermo-electric force is greater.

Thermal Conductivity.

From the intimate relations existing between electrical and thermal conductivity—recently elucidated to a considerable extent by J. J. Thomson's corpuscular theory—the laws regulating electrical conductivity may be expected to hold also for thermal conductivity. One well-defined relation is that the thermal conductivities of metals are nearly proportional to their electrical conductivities. This rule was demonstrated by the work of G. Wiedemann.[1] In the following table we give some values obtained by Wiedemann for the copper-zinc and tin-bismuth alloys. The coefficient of thermal conductivity is given under κ, that of electrical conductivity under λ.

Alloys.	κ	λ
Cu-Zn — ratio 8 : 1	27·3	25·5
,, ,, 6·5 : 1	29·9	30·9
,, ,, 4·7 : 1	31·1	29·2
,, ,, 2·1 : 1	25·8	25·7
Sn-Bi ,, 3 : 1	10·1	9
,, ,, 1 : 1	5·6	4·3
,, ,, 1 : 3	2·7	2

The thermal conductivity κ of certain binary alloys can be calculated according to F. A. Schulze [2] by the mixture rule; in the case of the bismuth-lead and bismuth-tin alloys, on the other hand, the value of κ is less than that calculated by this rule.

According to W. Voigt,[3] the determination of the ratio

[1] *Pogg. Ann.*, **108**, 393 (1859); *Ann. Chim. Phys.*, (3), **58**, 126 (1860); *Phil. Mag.*, (4) **19**, 243 (1860).
[2] F. A. Schulze, *D.-A.*, **9**, 555 (1902).
[3] *Wied. Ann.*, **64**, 95 (1898).

$\kappa : \kappa_1$ of the thermal conductivities of two substances in the case of heat flowing across the junction of two laminæ may be given by $\kappa : \kappa_1 = \tan \phi_1 : \tan \phi$, where ϕ, ϕ_1 are the angles formed by the directions of heat flow in the two substances with the normal to their line of separation.

The number of determinations made hitherto on the thermal conductivity of alloys is small. Among the most important researches bearing on the question of the occurrence of intermetallic compounds are those recently made by A. Eucken and G. Gehlhoff,[1] who have determined the conductivity of the cadmium-antimony alloys in which the compound CdSb (see Chapter V) occurs. They found that while for the metals the temperature coefficient of conductivity has a value approximately 1·3, for the compound the value is about 2·8. It must, however, be borne in mind that the antimony-cadmium compound approximates in character to a metalloid, which renders it impossible to draw general conclusions from these results. At present this branch of the subject is comparatively little understood, and what knowledge we possess does not permit us to make any generalisations. The methods employed for the determination of thermal conductivity are as various as the theoretical principles underlying them.[2]

A physical constant of considerable importance is the ratio between the electrical conductivity λ and the thermal conductivity κ; it has been used, for example, in the study of the compound SbCd by Eucken and Gehlhoff (*loc. cit.*). This ratio, it can be argued, is influenced by temperature and increases proportionately to it. Some determinations of the ratio $\frac{\lambda}{\kappa}$ between 600° and 0° have shown that it has an almost constant value for metals and is approximately 1·367. The value becomes greater for alloys in which solid solutions or compounds occur.

[1] *Ber.*, **14**, 169 (1912).
[2] *Cf.* Chwolson, *Traité de Physique*, Vol. III., pp. 348 *et seq.* Paris, 1909.

The temperature coefficient of thermal conductivity has been found to be *positive* for aluminium, gold and platinum and for certain binary and ternary alloys, such as manganin and constantin ; *negative* values are given by bismuth, tin, lead, cadmium, copper, silver, zinc, iron and nickel.

Thermal Dilatation.

The study of thermal dilatation has only been applied to a limited degree to metallic alloys. The investigations of

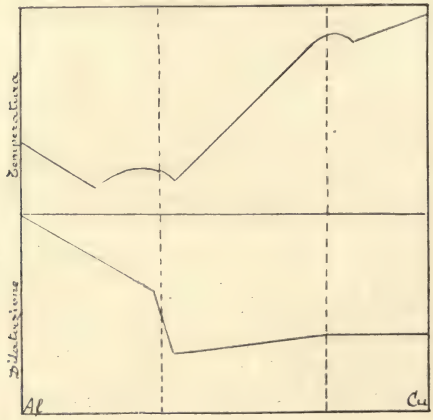

FIG. 30.

Matthiessen [1] and Le Chatelier [2] have led to certain generalisations of value.

For a solid isotropic body, length is in general a function of temperature and may be expressed by the formula :—

$$l = l_0 (1 + At + Bt^2 + Ct^3 + \ldots.),$$

where l and l_0 indicate the length of the body at $t°$ and $0°$

[1] *Pogg. Ann.*, **130**, 50 (1867) ; *Phil. Trans.*, **156**, 861 (1866) ; *Phil. Mag.*, (4), **31**, 149 (1866) ; **32**, 472 (1866).

[2] *C. R.*, **108**, 1096 (1889) ; **128**, 1444 (1899) ; **129**, 331 (1899). *Cf.* also by the same author : *Sur les Propriétés des Alliages* in the volume *Contribution à l'Étude des Alliages*, p. 387. Paris, 1901.

respectively. A, B, C, etc., are constants. The coefficient of dilatation between 0° and $t°$ is expressed by

$$\alpha = A + 2\,Bt + 3\,Ct^2 + \ldots.$$

This coefficient has been principally used for the study of metallic alloys. Matthiessen, in the investigations mentioned, found that the dilatation of an alloy can be calculated by the mixture rule, for it is equal to the sum of the dilatations of its components. This conclusion is, however, only valid in the cases in which the alloys are uniform conglomerate mixtures. Polymorphic transformations, for example, are always accompanied by discontinuities in the dilatation curves.

A variation in the dilatation curve is to be attributed to the formation of solid solutions or of compounds. The presence of a compound, as Le Chatelier found, is indicated by the occurrence of a maximum in the dilatation curve. Le Chatelier studied the dilatation of the copper-antimony and copper-aluminium alloys, in which the compounds $SbCu_2$, $SbCu_4$, $AlCu_3$ and Al_2Cu appear.

Comparing the fusion curve with the dilatation curve of the system CuAl, it is seen that at the first maximum in the one curve there corresponds a discontinuity in the other curve.

The methods used for the determination of dilatometric data are various,[1] but will not be set out in the present volume. It may be mentioned that Tammann in collaboration with Sahmen [2] has described a very accurate dilatometer. The investigations of Svedelius [3] may also be mentioned. He has noted that in the cooling as well as in the heating of steel there occurs at about 660° and 730° an abnormal contraction which is connected with the carbon content of the metal.

Guillaume [4] has also worked on the alloys of nickel.

[1] See Chwolson, *Traité de Physique*, Vol. III., pp. 96 *et seq.*, and Guillet, *Étude Théorique des Alliages Métalliques*, p. 147. Paris, 1904. Le Chatelier describes an optical method. *Cf. Contrib. à l'Étude des Alliages*, p. 387.

[2] *Ann. d. Phys.*, (4), **10**, 879 (1903).

[3] *Phil. Mag.*, (5), **46**, 173 (1898).

[4] *C. R.*, **124**, 176, 752 (1897); **125**, 235 (1897): **136**, 303, 356 (1903). *Jour. de Phys.*, (3), **7**, 264 (1898).

Hardness.

Although it is difficult to give an exact scientific definition of the hardness of a body, it has come to mean the resistance which it opposes to a force acting on its surface.

It has been found that the hardness of alloys is proportional to the composition when the constituents are present in the form of a conglomerate. The presence of solid solutions or definite compounds has, however, a considerable influence on the form of the hardness-composition curve. The most important investigations on this property in relation to the composition of binary metallic alloys are those of Kurnakoff and his co-workers.[1] Their studies have resulted in a rapid development of this method of investigation, which often furnishes reliable evidence as to the composition of alloys.

Before describing the applications of the study of hardness to metallic alloys in which compounds occur, we may mention that this physical property has often claimed the attention of investigators. Thus, J. R. Rydberg[2] found that the hardness of elements is a periodic function of their atomic weights. He has given the values for all the elements in the order of Mendeléjeff's classification.

The values have been expressed by means of Moh's scale of hardness, in which the following are the degrees :—

1. Talc.
2. Gypsum.
3. Calc-spar.
4. Fluor-spar.
5. Apatite.
6. Orthoclase.
7. Quartz.
8. Topaz.
9. Corundum.
10. Diamond.

[1] Kurnakoff and Zemczuzny, *Zeit. anorg. Chem.*, **60**, 1 (1908); **64**, 149 (1909) Kurnakoff and Pushin, *ibid.*, **68**, 123 (1910). Kurnakoff and Smirnoff, *ibid.*, **72**, 31 (1911).

[2] *Zeit. phys. Chem.*, **33**, 353 (1900).

HARDNESS OF THE ELEMENTS (RYDBERG).

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Li	Be	B	C	N	O	F	
·6	(3)	9·5	10	(·2)	(·5)	(·2)	
Na	Mg	Al	Si	P	S	Cl	
·4	2	2·9	7	·5	2	(·4)	
K	Ca	Si	Ti	V	Cr	Mn	Fe Co Ni
·5	1·5	(3)	(4)	(6)	9	(6)	4·5 (5) (5)
Cu	Zn	Ga	Ge	As	Se	Br	
3	2·5	1·5	(3)	3·5	2	(·6)	
Rb	Sr	Y	Zr	Nb	Mo		Ru Rh Pd
·3	1·8	(3)	(4)	(6)	(8·5)		6·5 (6) 4·8
Ag	Cd	In	Sn	Sb	Te	I	
2·7	2	1·2	1·8	3	2·3	(·8)	
Cs	Ba	La	Ce	Di			
·2	2	(3)	(3)	(5)			
				Ta	W		Os Ir Pt
				(7)	(9)		7 6·5 4·3
Au	Hg	Tl	Pb	Bi			
2·5	1·5	1·2	1·5	2·5			

The scale of hardness devised by F. Auerbach [1] is more rational and expresses the property in absolute degrees. Auerbach's method is based on the following argument which had previously been elaborated by H. Hertz.[2] If a convex surface of a body is compressed against a plane surface of the same body or another body a circular surface of contact will be produced, and the pressure upon this circular area eventually produces a rupture about its centre. As a measure of hardness, Auerbach takes the pressure P on the circle of contact (whose magnitude is determined microscopically) at the moment of rupture. If q be the area of the circle of contact and D its diameter,

$$P_1 = \frac{3}{2}\frac{P}{q} = \frac{3}{2\pi}\frac{P}{\left(\frac{D}{2}\right)^2} = \frac{6}{\pi}\frac{P}{D^2}.$$

P_1 varies inversely as the cube root of the radius of the com-

[1] *Wied. Ann.*, **43**, 60 (1891); **58**, 380 (1896).
[2] *Crelles Journal*, **92**, 156 (1882). *Gesamte Werke*, Vol. I., p. 155.

pressed sphere. The values obtained by Auerbach for the fundamental substances on Moh's scale are the following expressed as kilograms per square millimetre :—

1. Talc	5.	6. Orthoclase	237.
2. Gypsum	14.	7. Quartz	308.
3. Calc-spar	92.	8. Topaz	525.
4. Fluor-spar	110.	9. Corundum	1,150.
5. Apatite	170.	10. Diamond	?

According to Bottone [1] the hardness of metals is proportional to $\frac{d}{m}$ where d is the density and m the atomic weight of the metal. E. Benedicks,[2] in a later paper, in which the hardness of alloys and metals is studied from a general and theoretical point of view, examines Bottone's results, from which, as shown, he deduces the formula—

$$D = \kappa \frac{d}{m}.$$

The ratio $\frac{d}{m}$ is called by Benedicks the atomic concentration. In this property of solid bodies it is easy to trace an analogy with gases [3] for which according to Avogadro's law the density is proportional to the atomic concentration at a given temperature.

Variation of Hardness with the Composition of Alloys.

It has already been said that in binary alloys formed of simple conglomerates, the hardness varies almost always in a linear manner with the composition ; but, in practice, small deviations may be noted. Considering, however, that the observations are not always made under comparable con-

[1] *Chem. News*, **27**, 215 (1873).
[2] *Zeit. phys. Chem.*, **36**, 529 (1901).
[3] Benedicks calls attention to this analogy, which is indeed not the only analogy existing between different states of matter.

ditions and that the mode of preparation of an alloy has an influence on its hardness, such deviations do not greatly invalidate the general conclusion. Fig. 31 shows the form of the hardness curve where the alloys are composed of simple conglomerates. The hardness varies in a linear fashion between the pure components A and B, whose hardness is represented by A' and B'.

The case is different where alloys are constituted of isomorphous mixtures (solid solutions) or contain one or

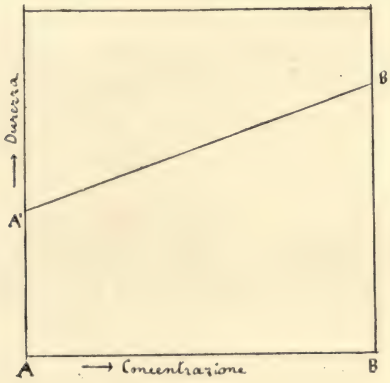

FIG. 31.

more definite compounds. The investigations of Kurnakoff already noted have not only embraced such cases but also cases in which a compound forms solid solutions with the components.

Kurnakoff's first rule for the hardness of isomorphous mixtures is that the property increases so as to reach a maximum for the median composition of the series of mixed crystals. This is shown in Fig. 32.

Tammann [1] has given a rational explanation of this

[1] *Cf.* Tammann, *Ueber die Beziehungen zwischen den inneren Kräften und Eigensch. der Lösungen*, p. 35 (1907); also *Lehrb. d. Metallographie*, p. 332.

behaviour. He supposes that in a given mixture the forces of attraction between dissimilar molecules are greater than

FIG. 32.

those between similar molecules. From this it follows that for liquids, the internal pressure, resulting from the sum of the forces of attraction per unit surface, is increased by the

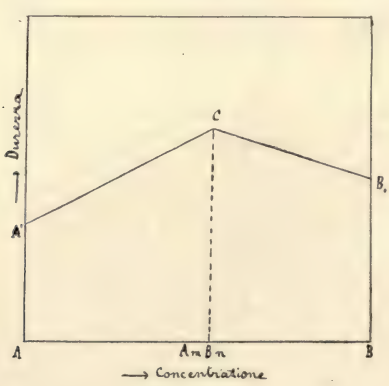

FIG. 33.

addition of another substance, and this must be the case with alloys. According to Tammann the attraction of two dissimilar molecules is greater both in the isotropic and in the anisotropic state.

When the formation of a compound takes place between two metals, the hardness increases and the maximum corresponds to the composition of the compound. The curve representing this behaviour consists therefore of two straight lines starting from points representing the hardness of the components and intersecting in a maximum point (Fig. 33).

The following table, giving the hardness of various intermetallic compounds, illustrates this point. The values for the pure components are also given. Hardness is given in degrees on Moh's scale.

Compounds.	Hardness of		
	Compound.	Components.	
Mg_2Sn	3·5	Mg — 2	Sn — 1·8
Mg_2Pb	3·5	,,	Pb — 1·5
$MgCu_2$	4·5	,,	Cu — 3
Mg_2Cu	4·5	,,	,,
Zn_2Cu	4·5	Zn — 2	,,
Cu_3Sn	4·5	Sn — 1·8	,,
Cu_3P	6 ±	P — ·5	,,
Cu_3Sb	4·5	Sb — 3	,,
CdSb	3·5	,,	Cd — 2
CoSb	5·5	,,	Co — 4±
NiSb	5 — 5·5	,,	Ni — 4±
CoSn	5·5	Sn — 1·8	Co — 4±
$CoSn_2$	5·5	,,	,,
$PbSb_2$	5·5	Sb — 3	Pb — 1·5
Ni_5As_2	6·5	Ni —4 ±	As — 3·5
Ni_5P_2	5·5	,,	P — ·5
PtSn	5·5	Pt — 4·3	Sn — 1·8
$NaCd_2$	>.3	Na —· 4	Cd — 2
Na_2Pb	2·5	,,	Pb — 1·5
NaPb	3 ±	,,	,,
NaSn	3 ±	,,	Sn — 1·8

When a compound forms solid solutions with the components, the hardness curve differs from the preceding cases described. Here two maxima appear and a point of intersection. The maxima correspond to the formation of mixed crystals and the point of intersection of the two branches to the compound (see Fig. 34). Kurnakoff and Smirnoff [1] have classified the hardness curves for alloys in which, in addition to the compound, solid solutions are formed. We

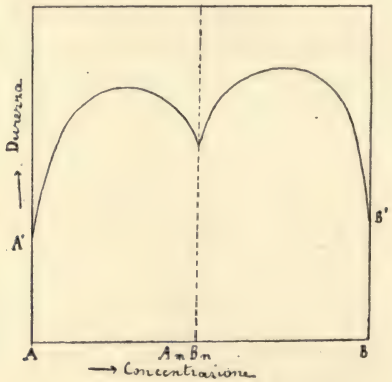

FIG. 34.

have discussed the question of compounds of variable composition in Chapter III. Kurnakoff and Smirnoff divide the cases in question into two groups: (1) compounds which are not dissociated either in the liquid or the solid state; and (2) compounds which dissociate on fusion. We will examine more closely the significance of this classification.

Group 1.—These compounds belong to the category of hylotropic phases mentioned by Ostwald.[2] Two types are

[1] *Zeit. anorg. Chem.*, **72**, 31 (1911).
[2] *Zeit. f. Elektrochemie*, **10**, 572 (1904).

distinguished ; in the first, (*a*), the compound forms a continuous series of solid solutions with the components ; in the

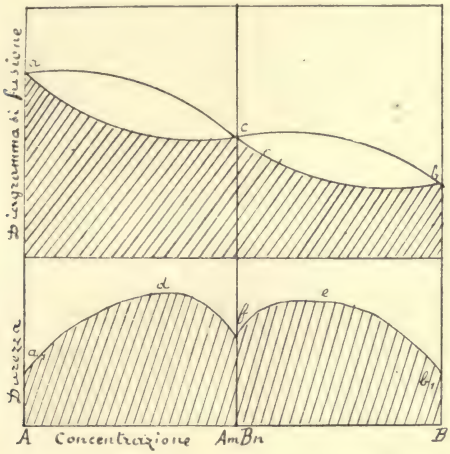

FIG. 35.

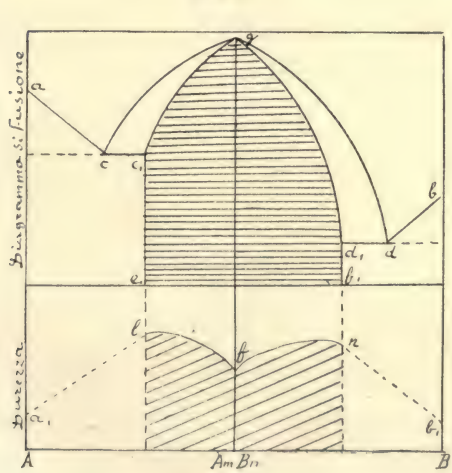

FIG. 36.

second, (*b*), the compound forms solid solutions only to a limited extent.

TYPE (*a*).—This case is shown in Fig. 35, where *c* represents the melting point of the binary compound $A_m B_n$.

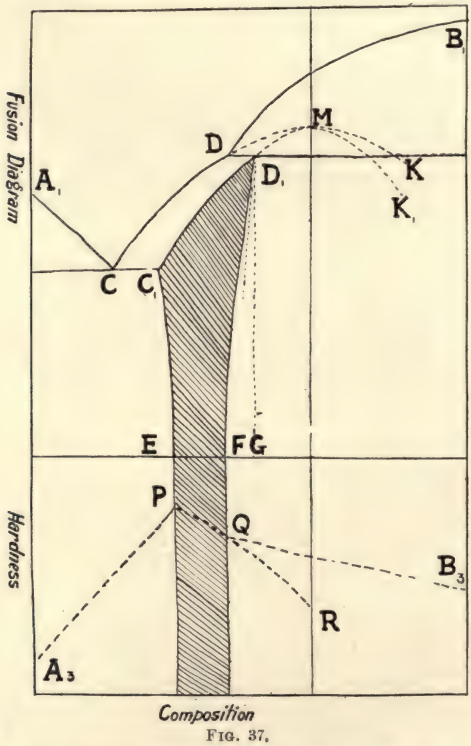

FIG. 37.

This may be between that of the two components, as in the diagram, or even above or below them. The two systems of isomorphous mixtures $A + A_m B_n$ and $A_m B_n + B$ are represented by the two curves $a_1 d f$ and $f e b_1$ with maximum points in *d* and *e*. The minimum *f* corresponds to the com-

pound $A_m B_n$; this may be found also above a_1 and b_1, *i.e.*, the hardness of the compound $A_m B_n$ may exceed that of the components.

TYPE (*b*).—As was said, this type is characterised by a gap in the series of solid solutions. The compound (see Fig. 36) shows a maximum and forms solid solutions with excess of A and B in the region limited by the lines $e_1 c_1 g d_1 f_1$. The curve $l f n$ represents the variations of hardness in the interval of concentration $e_1 f_1$. The presence of solid solutions is accompanied by an increase in hardness and the two branches intersect in f, which represents the compound.

Group 2.—The behaviour of substances of this group is represented by Fig. 37. The compound melts at the point D and gives rise to the component B. D_1 which is the point of intersection of the horizontal $D D_1$ with the curve $C_1 M$ (which indicates the concentration of the solid solutions) represents the highest temperature at which the solid phase of the compound is stable. The branches $D M K$ and $D_1 M K_1$, which pass through the obscured maximum M, belong to the labile state of the compound.

Discontinuities occur at P and Q corresponding to changes in the hardness of the solid solutions with A and B.

The measurements of hardness made up to the present have been carried out either by means of the *sclerometer* or by Brinell's method.

Compressibility.

In direct relation with the hardness of a substance is the property of compressibility under pressure. Kurnakoff has used this property also in his investigations on the variation of the physical properties of alloys with their composition (see Bibliography, p. 88). Since this property is intimately connected with hardness there is no purpose in giving any particular detailed treatment of the subject. It is sufficient to mention that in isomorphous mixtures the compressibility

as well as the hardness, exhibits a maximum on the curve showing its relation to composition. The apparatus used by Kurnakoff is described in the first memoir,[1] and has been used for conglomerates of mixed crystals, metals, inorganic salts and organic substances. Among the substances thus examined are the thallium-lead and thallium-bismuth alloys, binary mixtures of silver chloride and bromide, potassium iodide and bromide, stearic and palmitic acids, p-dichlorobenzene and p-dibromobenzene.

The researches of Kurnakoff on the compressibility of the thallium-bismuth alloys are above all worthy of note since they have served in the determination of the irrational maximum of the compound of variable composition whose formula is approximately Bi_5Tl_3 (see Chapter V).

Crystalline Form of Binary Compounds.

Comparatively few intermetallic compounds have been studied crystallographically, so that we possess very little definite information on this subject. Studies are also wanting on the relations between crystalline form and degree of saturation of compounds.

The crystalline forms of metals are generally known; they crystallise most often in the regular or the hexagonal-rhombohedral systems. Silver, cadmium, iron, iridium, mercury, nickel, gold, osmium, lead, platinum, palladium and others of the platinum group belong to the regular system. The latter are, however, dimorphous and crystallise also in the hexagonal system. Arsenic, beryllium, antimony, bismuth, magnesium, tellurium and zinc crystallise in the hexagonal system. Potassium and sodium are tetragonal, while tin crystallises in the tetragonal and also in the rhombohedral system. Zirconium is monoclinic. The intermetallic compounds given in the following table have been studied crystallographically :—

[1] *Zeit. anorg. Chem.*, **60**, 22 (1908).

Compound.	Crystalline system.	Compound.	Crystalline system.
$NaCd_2$	Cubic	$FeZn_7$	Hexagonal
Mg_2Sn	,,	NiAs (Niccolite)	,,
Ag_2Te	,,	NiSb	,,
Ag_4Zn	,,	Bi_2Te_3 (Tetradimite)	,,
Ag_2Zn	,,	Ni_2Te_3 (Melanite)	,,
AgZn	,,	Cd_2Sb_2	Orthorhombic
Cu_6Ni	,,	$FeSb_2$	,,
Cu_3Zn	,,	Ag_2Sb (Dyscrasite)	,,
CuZn	,,	ZnSb	,,
$CuZn_3$	,,	$FeAs_2$ (Löllingite)	,,
PbTe (Altaite)	,,	$NiAs_2$ (Rammelsbergite)	,,
$CoAs_2$ (Smaltite)	,,	$CoAs_2$ (Safflorite)	,,
$NiAs_2$ (Cloantite)	,,	$CeAl_4$	,,
$CoAs_3$	,,	$LaAl_4$	,,
$PbAs_2$ (Sperrilite)	,,	$ThAl_4$	,,
$CuSn_2$	Hexagonal	$FeAl_3$	Monoclinic
CuSn	,,	$AsSn_2$	Tetragonal
Cu_4Sn	,,		

Our information on other intermetallic compounds is very limited. Groth, in his *Chemische Krystallographie*,[1] gives certain data about artificially prepared compounds, whose crystallographic characters are not yet well understood.

(*a*) *Bivalent Metals.*—The compounds of beryllium and magnesium with monovalent metals have not yet been studied crystallographically.

The zinc compounds with copper and silver described by Behrens [2] have been given in the above table. The amalgams of lithium, sodium and potassium are very numerous ; they crystallise partly in needles and partly in hexahedral forms. Some of the copper, silver and gold amalgams crystallise in the cubic system. The compound $CoHg_5$ was obtained in prisms which, however, were not examined very exactly. Crystalline amalgams exist of barium and strontium.

[1] Vol. I., pp. 43 *et seq.*, 1906.

[2] *Gefüge d. Metalle u. Legierungen*, pp. 46 and 100. Hamburg and Leipzig, 1894.

(*b*) *Trivalent Metals*.—Behrens [1] and Guillet [2] obtained the following crystalline compounds of copper and aluminium: Cu_3Al, CuAl and Cu_2Al_3; Petrenko [3] obtained two crystalline compounds of aluminium and silver, namely, Ag_3Al and Ag_2Al; Heycock and Neville [4] prepared from aluminium and gold, Au_4Al, Au_2Al and $AuAl_2$; but the crystalline form of all these compounds was not determined.

Thallium forms compounds with the monovalent metals in which it behaves as a heavy metal. Kurnakoff,[5] from the thallium-sodium and thallium-potassium alloys, obtained the compounds NaTl and KTl, the former in the form of three-rayed aggregates and the latter in the form of cubes. The thallides of the bivalent metals, of which some of magnesium are known, are very little recognised.

(*c*) *Tetravalent Metals*. — In addition to the *stannides* shown in the preceding table, Groth [6] refers to the compound Cu_3Sn which crystallises in small prisms. The compound $CuSn_2$ was described by Miller [7] and Rammelsberg [8] as occurring in hexagonal prisms. The stannides of silver have not yet been isolated nor have the compounds with gold, AuSn, $AuSn_2$ and $AuSn_4$ described by Vogel.[9]

Copper and silver form double *plumbides*: Curlt [10] describes the compound $CuAgPb_2$ as forming regular octahedra. The gold *plumbides* described by Vogel,[11] Au_2Pb and AuP_2 crystallise respectively as rhombs and long needles.

Among the *stannides* of iron, Fe_4Sn, Fe_3Sn, FeSn and

[1] *Op. cit.*, p. 107.
[2] *C. R.*, **133**, 684 (1901).
[3] *Zeit. anorg. Chem.*, **46**, 49 (1905).
[4] *Trans. Roy. Soc.*, 194, 201 (1900).
[5] *Zeit. anorg. Chem.*, **30**, 86 (1902).
[6] *Op. cit.*, p. 46.
[7] *Phil. Mag.*, 1835, p. 107, and *Pogg. Ann.*, **36**, 478.
[8] *Zeit. anorg. Chem.*, **46**, 60 (1905).
[9] *Pogg. Ann.*, **120**, 34 (1863).
[10] *Uebers. d. pyrogen. Kunstl. Mineralien*, Freiberg (1857), p. 17.
[11] *Zeit. anorg. Chem.*, **45** (1905).

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$FeSn_2$, described by Headden and Stevanovitch,[1] are known. The bistannide crystallises in long needles.

Few stannides of the trivalent metals are known: the stannides of aluminium, $AlSn_4$ and AlSn, prepared by Guillet[2] have not been studied crystallographically.

It is worth while recording here the observations of Barlow and Pope[3] on a regularity in the crystalline form of binary compounds formed by the union of elements of equal valency; such compounds crystallise in the cubic or hexagonal systems and generally in classes with a lesser degree of symmetry. According to these authors, the molecules which form the homogeneous structure which is the crystal are constituted of similar atoms. But beyond this similarity of the atoms it is possible to think of other factors which influence crystalline form. The homogeneity or uniform structure of the crystal is conditioned by two opposing forces: (*a*) a repulsive force due to the kinetic energy of the atom, and (*b*) an attractive force varying as the square of the distance between the atoms.

Concerning this question of the nature of the forces which maintain the component atoms of crystals in equilibrium, Nernst and Lindemann[4] have recently stated that the attractive force is identical with that of chemical affinity. This, of course, throws additional light on the regularity noted by Barlow and Pope.

Natural Intermetallic Compounds.

Among the intermetallic compounds studied, the majority are homopolar, resulting from the action of unitary forces. Compounds of this group are not ionisable and exhibit in their properties the properties of their constituent elements. All intermetallic compounds, however, are not formed by

[1] *Zeit. f. Krystall*, **40**, 327 (1905).
[2] *C. R.*, **133**, 935 (1901).
[3] *Trans. Chem. Soc.*, **89**, 1675 (1906).
[4] *Cf.* Nernst, *The Theory of the Solid State*, p. 4. London, 1914.

the union of homopolar elements. Indeed, certain metalloidal elements are able to form with metals true alloys having markedly metallic characters. Among such metalloidal elements are carbon, silicon, boron, tellurium, selenium, phosphorus and arsenic.

The natural intermetallic compounds are generally heteropolar. Native metals are few in number and chiefly alloys of the elements of the iron group (iron, cobalt and nickel) and of platinum, mercury, copper, silver and gold. Among these metals those with the highest melting points tend to form solid solutions. Thus gold forms solid solutions with silver (*electrum*), palladium and rhodium, osmium and iridium from iridosmin ; and lastly, in meteorites, nickel and iron are found united in solid solutions.

The following tellurides occur naturally :—

AgTe — Silvanite and empressite.	$AgAuTe_2$ — Krennerite.
Ag_2Te — Hessite.	AgAuTe — Muthmannite.
Ag_4Te — Stutzite.	$HgAu_2Ag_6Te$ — Kalgoartite.
$AuTe_2$ — Colaverite.	Bi_2Te_3 — Tetradimite.
$(AgAu)_2$ — Petzite.	HgTe — Coloradoite.
$(AgAu)_2Te_6$ — Goldschmite.	PbTe — Altaite.
	NiTe — Melanite.

Silvanite, colaverite and krennerite, though recognised as definite minerals have not been encountered in the study of fusion diagrams. Pellini [1] has found recently in the study of the system silver-gold-tellurium by thermal analysis the compound $(AgAu)_3Te_2$, which has not been discovered among the gold minerals hitherto investigated. Empressite was found recently by M. W. Bradley [2] ; Pellini and Quercigh [3] have also noted the existence of the compound AgTe by thermal methods.

Stutzite is probably a mixture of Ag_2Te and silver, while melanite probably contains the compound NiTe.

[1] *Gazz. Chim. Ital.*, **45**, I., 47 (1915).
[2] *Journ. of Science*, **38**, 163 (1914).
[3] *R. Acc. Lincei*, **19**, II., 415, 445 (1910).

A bismuth telluride must also be mentioned whose composition is not exactly known and which has been called Joseite.

The following native antimonides and arsenides occur :—

Ag_3Sb — Dyscrasite.
Ag_6Sb — (variety of dyscrasite).
Cu_6Sb — Horsfordite.
NiSb — Breithaufite.
Ag_3As — Arsenoargentite.
Cu_3As — Domeichite.
Cu_6As — Algodonite.
Cu_9As — Whitnegite.

$FeAs_2$ { Löllingite. Arsenoferrite.
Fe_3As_4 — Lemopyrite.
$CoAs_2$ { Smaltite. Safflorite.
$CoAs_3$ — Skutterodite.
NiAs — Niccolite.
$NiAs_2$ { Chloantite. Rammelsbergite.
$PbAs_2$ — Sperrylite.
$Co(AsBi)_3$ — Bismuthosmaltite.

A selenide of bismuth, guanajnatite, exists of the composition Bi_2Se_3 ; silvanite, to which at first the formula Bi_3Se was assigned,[1] has been since[2] recognised to be a mixture of Bi_2Se_3 and bismuth. N. Parravano,[3] in a study of the system Bi—Se, has demonstrated the existence of two selenides, Bi_2Se_3 and BiSe.

The mineral naumannite, Ag_2Se, found in nature, is isomorphous with argentite and hessite. Naumannite and hessite are found in isomorphous mixtures in the mineral aguilarite. The system silver-selenium has recently been studied by Pellini.[4]

Some of the minerals here mentioned and at present regarded as definite compounds are probably isomorphous mixtures. Although a mineral may have a uniform structure and a constant composition it is not always a true chemical individual. In this connection it is well to bear in mind that several native compounds have not been

[1] *Zeit. f. Kryst.*, **1**, 499 (1877).
[2] *Ibid.*, **6**, 96 (1888).
[3] *Gazz. Chim. Ital.*, **43**, I., 201 (1913).
[4] *Ibid.*, **45**, I., 533 (1915).

recorded in the thermal study of the mixtures of their constituent elements.

The recent developments of the study of heterogeneous equilibria and the introduction of Tammann's method into physico-chemical research, although they have not led to a complete elucidation of this important aspect of mineralogy, have nevertheless furnished powerful means of investigation which promise much for the future.

CHAPTER V.

Homopolar Intermetallic Compounds.

Compounds of the Elements of Group I. among themselves.

1*st sub-group*.—The only compound known in this sub-group is that formed by sodium with potassium. The *sodium-potassium* compound has the formula Na_2K. The system has been studied by Kurnakoff and Pushin [1] and the diagram is shown in Fig. 38. According to Kurnakoff the curve shows a break corresponding to 40 per cent. of potassium at 638° ; this may demonstrate the existence of a compound of the formula Na_2K or Na_3K_2. Bornemann [2] on the other hand believes that there are three species of mixed crystals between the two pure components. The branches of the curve Na α and Kγ are convex to the axis representing concentration, showing that the two metals instead of separating in the pure state form solid solutions. According to Bornemann the presence of a strongly dissociated compound of the type Na_nK must be admitted. If we hold with Kurnakoff that the break on the fusion curve corresponds to the compound, so that the crystals β saturated with sodium are identical with the compound, we may have Na_2K or Na_3K. The composition represented by Na_3K is near a point of arrest. Bornemann holds that it should be characterised by a more decided point of arrest and that the compound is probably Na_2K.[3]

Lithium is miscible with sodium and potassium with

[1] *Zeit. anorg. Chem.*, **30**, 109 (1902).
[2] *Die binären Metallegierungen*, Halle (1905), p. 7.
[3] *Cf.* also Van Bleiswyk, *Zeit. anorg. Chem.*, **74**, 152 (1912).

difficulty.[1] Nothing is known of the behaviour of lithium and sodium with cæsium and rubidium.

2nd sub-group.—Copper, silver, and gold give alloys with

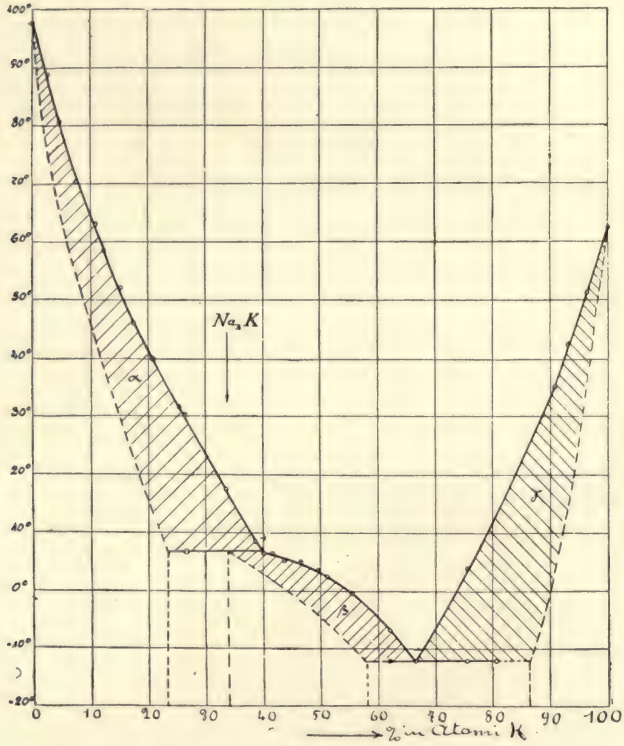

FIG. 38.

each other with complete or partial formation of solid solutions. Sodium alone among the elements of the first sub-group forms the compound $NaAu_2$. The system *sodium-*

[1] *Zeit. anorg. Chem.*, **67**, 183 (1910).

gold has been studied by Mathewson,[1] who has noted the formation of a compound. Silver and copper on the contrary do not combine with sodium, which, of course, is contrary to Tammann's rule.

The diagram (see Fig. 39) is fairly simple. At a concen-

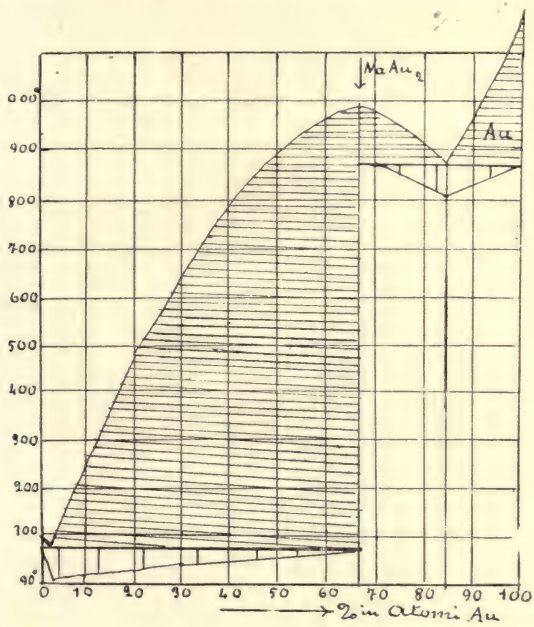

FIG. 39.

tration of 3·6 per cent. of gold there is an eutectic point; at 66·6 per cent. of gold and at 989° there is a maximum corresponding to the compound $NaAu_2$. A second eutectic between the compound and gold occurs at 876°. There is no indication of the formation of solid solutions in the diagram. The compound $NaAu_2$ is chemically very resistant and exhibits a considerable degree of hardness.

[1] *Intern. Zeit. f. Metall*, **1**, 85 (1911).

Compounds of Elements of Group II. with each other.

1*st sub-group.*—The behaviour of the metals of this sub-group has not been studied as yet.

2*nd sub-group.*—Magnesium forms with zinc the compound $MgZn_2$; with cadmium it forms the compound MgCd, and with mercury a compound whose composition is not yet determined.

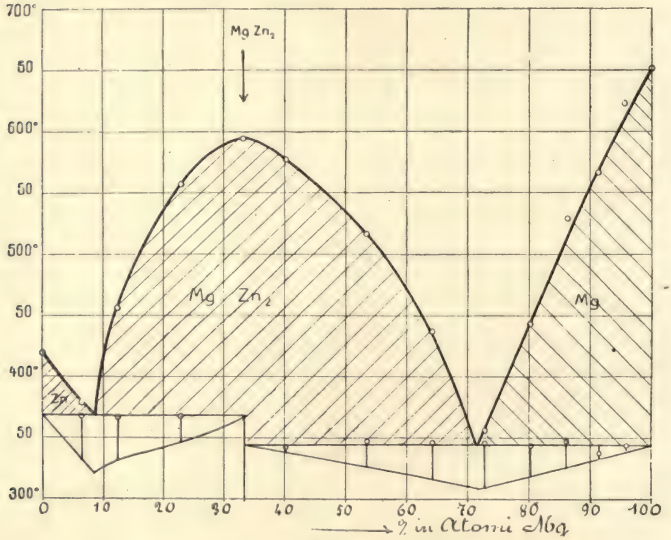

FIG. 40.

Magnesium-zinc.—The system magnesium-zinc has been investigated by Boudouard [1] and Grube.[2] From the diagram constructed by the latter, who has traced cooling curves from 650° to 250° (see Fig. 40), Grube inferred the existence of a compound $MgZn_2$, which is formed at 590°, and at 33 per cent. magnesium. A small deviation noted

[1] *C. R.*, **139**, 424 (1904). *Bull. Soc. Chim.*, (3), **31**, 1201.
[2] *Zeit. anorg. Chem.*, **49**, 77 (1906).

near the eutectic point between magnesium and $MgZn_2$ is due to the presence of magnesium or the compound, which must be attributed to super-cooling. Grube denies the formation of solid solutions on the one hand between the compound and magnesium, and on the other hand between zinc and the compound. Magnesium tends on first separation, if present in small quantity, to crystallise in dendritic forms. According to Boudouard the compound Mg_4Zn is also formed. This, however, is denied by Grube, arguing from the theory of heterogeneous systems, since the eutectic horizontals of

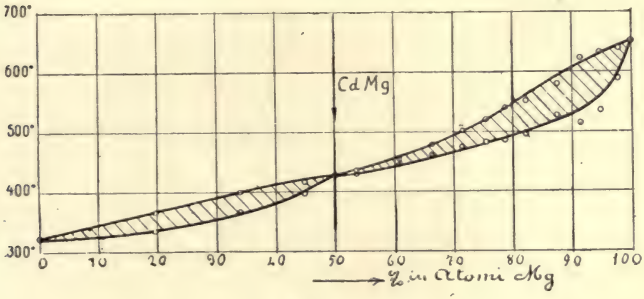

FIG. 41.

the compound $MgZn_2$ extend over the whole diagram. Microscopic analysis also excludes the formation of Boudouard's supposed compound.

The compound $MgZn_2$ is unattacked by water and air ; it has a brilliant white colour and is a little harder than its constituents. It is very brittle.

Magnesium-cadmium.—The system magnesium-cadmium has been investigated by Boudouard [1] and Grube.[2] According to Boudouard the compounds MgCd, Mg_4Cd and Mg_3Cd occur, while Grube only reports one compound, namely, MgCd. From the diagram (Fig. 41) he argues complete miscibility both in the liquid and solid states.

[1] *C. R.*, **134**, 1431 (1902). *Bull. Soc. Chim.*, (3), **27**, 854 (1902).
[2] *Zeit. anorg. Chem.*, **49**, 72 (1906).

Near 50 per cent. of cadmium the crystallisation interval between liquid and solid practically vanishes so that the liquidus and solidus curves touch.

Between 35·9 per cent. and 66·4 per cent. of magnesium the compound MgCd and the mixed crystals of the compound and its components undergo a transformation into another series of mixed crystals. By crystallising slowly, homogeneous alloys are obtained.

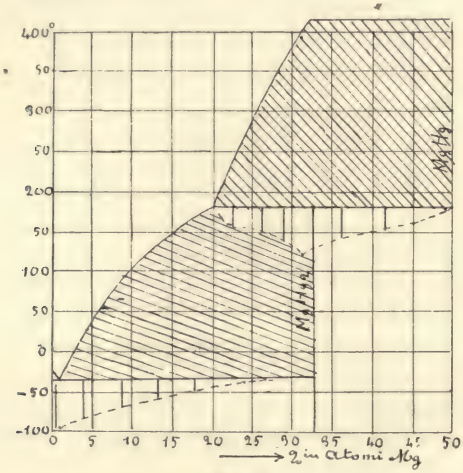

FIG. 42.

The compound MgCd is greyish-white in colour, a little harder than its constituents, and very resistant to water and moist air.

MAGNESIUM AND CALCIUM AMALGAMS.

Mercury-magnesium.—This system has recently been studied by L. Cambi and G. Speroni.[1] The two elements combine to form the compounds $MgHg_2$ and MgHg. The system has been investigated up to a concentration of 50 per

[1] *R. Acc. Lincei*, **24**, I., 734, 932 (1915).

cent. magnesium. Preliminary researches were made by Wanklin and Chapman[1] and by Kerp and Böttger.[2]

By addition of a very small quantity of magnesium the melting point of mercury is lowered (see Fig. 42). The diagram then rises in a curve to 168°, where there is a discontinuity corresponding to the compound $MgHg_2$. The existence of the compound MgHg has not been proved directly by the thermal method, for this series of observations

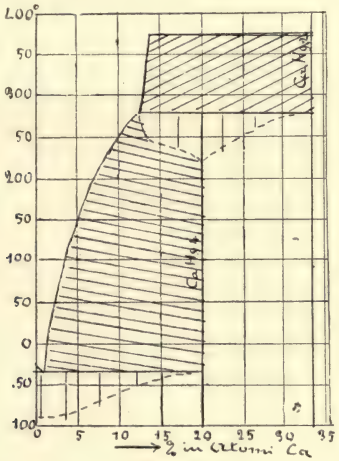

FIG. 43.

terminates at 5·08 per cent. by weight or 30 per cent. atomic of mercury. The amalgam with 32—34 per cent. atomic magnesium boils at 415°. Cambi has also studied the electromotive force of magnesium amalgams.

In 1904 Evans and Fetsch,[3] working on magnesium amalgam as a reducing agent, prepared a homogeneous amalgam corresponding to the formula $MgHg_2$ from one part magnesium and eighteen parts of mercury. The formation of

[1] *J. C. S.*, (2), **4**, 141 (1866).
[2] *Zeit. anorg. Chem.*, **25**, 33 (1900).
[3] *J. Am. C. S.*, **26**, 1158 (1904).

this compound is shown clearly by the thermal study of the system.

Mercury-calcium.—The affinity of calcium for mercury is very slight; at ordinary temperatures calcium dissolves slowly in mercury. The capacity for combination between the two metals has long been known, but the system has only been studied recently by Cambi and Speroni [1] who have shown the existence of the compound $CaHg_4$.

The diagram is shown in Fig. 43 and only extends to 33 per cent. atomic of calcium. The compound melts with decomposition at 266° C. Thermal analyses do not indicate the existence of any other compounds. Moissan and Chavanne [2] had previously described a compound of the formula $CaHg_2$ crystallising in hexagonal prisms. J. Schürger [3] recorded the existence of a crystalline compound $CaHg_5$ while J. Férée [4] described a compound Ca_3Hg_4 easily altered on exposure to air. Thermal analysis, however, renders the existence of the last three compounds very improbable.

Strontium-mercury.—Strontium like the other metals of the alkaline earths combines chemically with mercury. From the researches of Kerp and Böttger [5] the existence of the compound $SrHg_{12}$, in equilibrium with the liquid phase at 30°, appears established. It decomposes at 60° to 70° and has a silvery appearance. An amalgam of strontium containing 5·37 per cent. of this metal separates a crystalline phase at 81°. The system has not yet been investigated by thermal methods.

Barium-mercury.—Barium combines with mercury. Kerp[6] and Kerp and Böttger [5] isolated two amalgams of the composition $BaHg_{12}$ and $BaHg_{13}$ by electrolysis of a saturated solution of barium chloride, using a mercury cathode.

[1] *R. Acc. Lincei*, **23**, II., 599 (1914).
[2] *C. R.*, **140**, 125 (1905).
[3] *Zeit. anorg. Chem.*, **25**, 426 (1900).
[4] *C. R.*, **127**, 619 (1898).
[5] *Zeit. anorg. Chem.*, **25**, 1 (1900).
[6] *Ibid.*, **17**, 284 (1898).

$BaHg_{12}$ crystallises in silvery cubes which become oxidised in the air. The amalgam containing 5·34 per cent. of barium separates a crystalline phase at 99°.

The system has not yet been studied thermally.

Compounds of Calcium with Metals of the Second Sub-group.

Calcium-magnesium.—Calcium combines with magnesium, forming the compound Ca_3Mg_4. The system has been

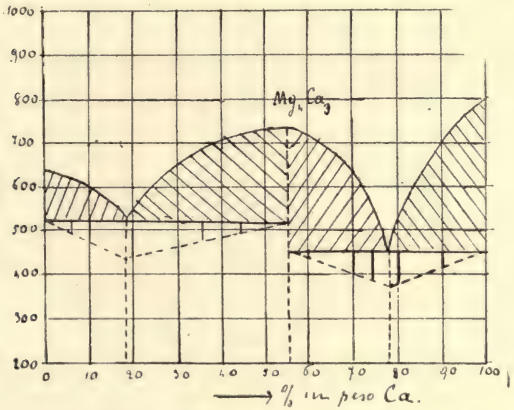

Fig. 44.

worked out by Baar.[1] The diagram traced by him (Fig. 44) shows that in the liquid state magnesium mixes with calcium in all proportions. The liquidus curve shows a maximum at 55 per cent. (by weight) of calcium and 715°. Here the compound Ca_3Mg_4 separates. Microscopic examination confirms the deductions made from the diagram, and shows that the compound exists in polyhedric crystals. The magnesium-calcium alloys, particularly those found in the vicinity of the composition of the compound, are

[1] *Zeit. anorg. Chem.*, **70**, 362 (1911).

very brittle; the alloys richer in calcium are more ductile. Exposed to air these alloys crumble to a grey powder in which are seen shining particles of the compound which is stable in air.

Calcium-zinc.—This system was studied by Donski,[1] who

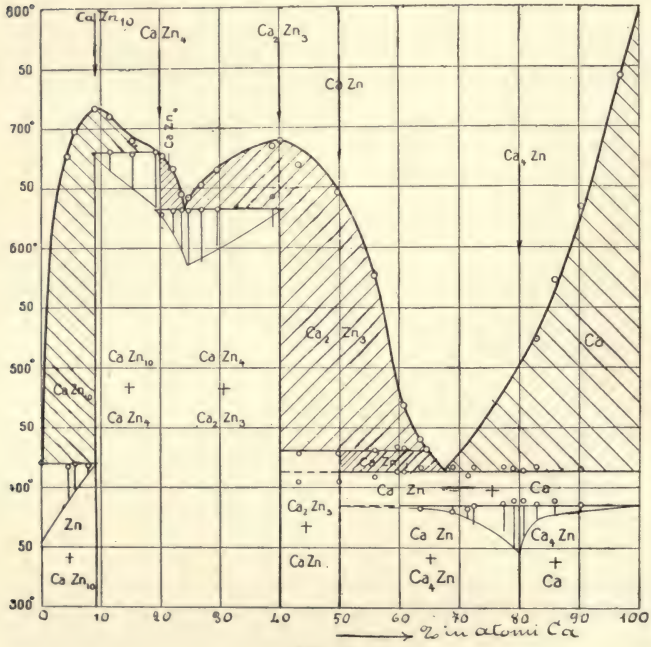

FIG. 45.

noted the formation of four compounds, namely, $CaZn_{10}$, $CaZn_4$, $CaZn_3$, and Ca_4Zn. On the fusion curve (see Fig. 45) between 9 and 20 per cent. Ca, there are distinct breaks at 677° and 717°. The compound $CaZn_{10}$ separates from its melt and from melts containing large proportions of it only

[1] *Zeit. anorg. Chem.*, **57**, 185 (1908).

after a super-cooling of about 16°. The second compound crystallises at 680° from melts containing 9·23 per cent. of calcium. This compound either melts without decomposition or else in melting splits off a small quantity of the compound $CaZn_{10}$. The first case occurs if the composition coincides with a point of transition, the second case when the composition is represented by points lying to the left of the said point. The curve rises again up to 40 per cent. calcium at a temperature of 688°, where the compound Ca_2Zn_3 separates. In the further course of the curve small arrests are noted at 431°, which probably correspond to a compound CaZn. Other arrests occur at 385°, between 52 and 84 per cent. of calcium with a maximal arrest at 80° calcium. This means that another species of crystal is formed having the formula Ca_4Zn.

The alloys from 0—6 per cent. calcium have the colour of pure zinc and are a little harder ; they are fairly stable in air, while those containing from 6—19 per cent. of calcium soon become grey. From 20—29 per cent. they decompose water, giving a black powder, and with greater energy the richer they are in calcium. The brittleness of these alloys increases from pure zinc up to 30 per cent. of calcium, diminishing thence as the proportion of the latter metal increases.

Calcium-cadmium.—Calcium combines with cadmium, forming the three compounds $CaCd_3$, CaCd and Ca_3Cd_2, according to Donski.[1] The curve (Fig. 46) shows a break at 615° and 24 per cent. of calcium and an eutectic point at 316°. The compound $CaCd_3$ separates only after a super-cooling of about 8°. At 685° from 27 to 84 per cent. of calcium, a lack of miscibility in the liquid state is noted. The compound CaCd forms at 50 per cent. of calcium, and arrests are observed corresponding to it. At about 515°, a new species of crystal separates which may be the compound of the formula Ca_3Cd_2, but this is not quite certain since the eutectic horizontal extends to 50 per cent. of calcium, whereas it

[1] *Zeit. anorg. Chem.*, 57, 193 (1908).

should extend only to 40 per cent. The last arrests are at 415° from 50—95 per cent. calcium, and correspond probably to mixed crystals.

The alloys containing up to 10 per cent. of calcium are fairly stable in the air and a little harder than calcium ; from

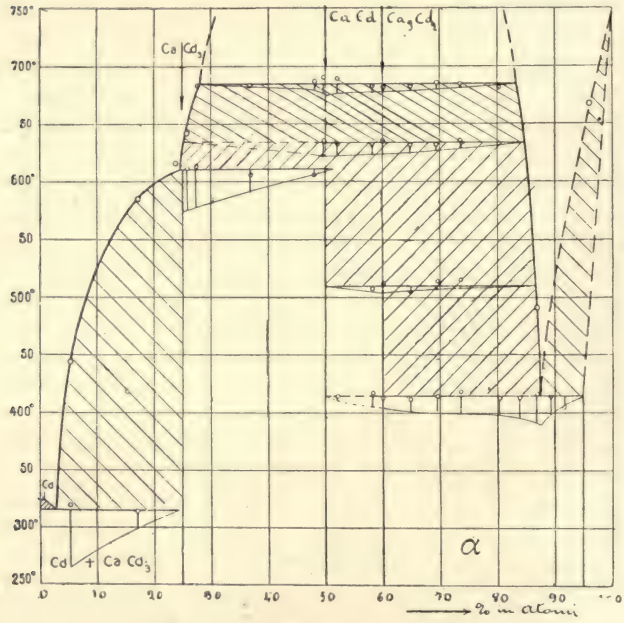

FIG. 46.

10—26 per cent. calcium they are less stable and decompose cold water ; alloys containing higher proportions of calcium are still more easily oxidised. Alloys become increasingly brittle from 10 up to 40 per cent. calcium, and then there is a decrease in this property.

Zinc does not form compounds with cadmium or mercury, nor mercury with cadmium.

Compounds of Elements of Group III. with each other.

The reciprocal behaviour of the elements of this group has not yet been closely studied. Tammann's first rule holds for this group. Gallium, indium and thallium form a complete series of solid solutions. Thallium and aluminium are not miscible in the liquid state according to Doerinckel.[1] It is probable that aluminium can combine with lanthanum.

Aluminium-lanthanum.—This system has not been studied thermally. Muthmann and Beck [2] by fusing together the two elements have obtained rhombic or monoclinic crystals, isomorphous with the compound of cerium and aluminium; their composition corresponds to the formula $LaAl_4$. The two metals react energetically on fusion. The compound has a white colour; its specific gravity is 3·923, which is approximately equal to the value calculated by the mixture rule.

Compounds of Elements of Group IV. with each other.

Two elements, namely, carbon and silicon, occur in this group, which are characterised by great capacity for combination. We shall have occasion later to deal at length with the carbides and silicides; they are of great importance on account of their relationship with compounds of a true metallic character. Silicon and carbon form a compound SiC called *carborundum*, which apart from its physical properties is of interest because it occupies a position intermediate between intermetallic compounds and the class of compounds to which sulphides and oxides belong.

Little is known at present of the alloys of titanium, zirconium, germanium and cerium with each other and with other elements of this group. Cerium combines with tin and lead.

Cerium-tin.—Cerium forms with tin the compounds Ce_2Sn, Ce_2Sn_3 and $CeSn_2$. The system has been investi-

[1] *Zeit. anorg. Chem.*, **48**, 188 (1906).
[2] *Ann. Chem.*, **331**, 51 (1904).

gated by Vogel.[1] As the diagram (Fig. 47) shows,[2] the three compounds melt at a temperature much above the melting points of their components. Thus $CeSn_2$ melts at 1135°, Ce_2Sn_3 at 1165° and Ce_2Sn at 1400°. At low temperatures the solubility of the first and the third compounds in their

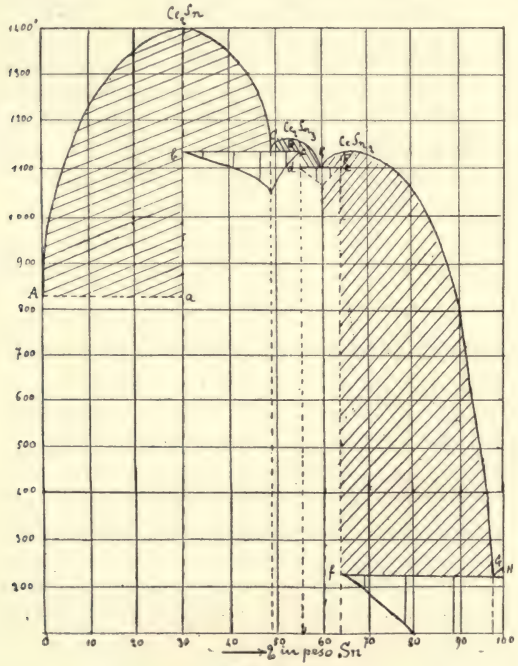

FIG. 47.

components is very small. Ce_2Sn separates out at about 30 per cent. of Sn, Ce_2Sn_3 at 56 per cent. Sn, and $CeSn_2$ at 64 per cent. Sn. The formation of the first two is accompanied by a small degree of super-cooling (up to 15°) which however is not observed in the case of $CeSn_2$.

[1] *Zeit. anorg. Chem.*, **72**, 319 (1911).

[2] In this diagram the proportions are by weight and not atomic proportions.

It is characteristic of these compounds that they are formed with great evolution of heat, with increasing intensity in the order $CeSn_2$, Ce_2Sn_3, Ce_2Sn.

All the alloys of cerium and tin, with the exception of those containing more than 80 per cent. of tin, are pyrophoric; above all, those containing $CeSn_2$. It should be added that these alloys are very hard and brittle.

Cerium-lead:—It appears from the researches of Muthmann and Beck [1] that cerium has the power of reacting with other metals with ease. They isolated by chemical means a compound $CeAl_4$; cerium and zinc, also, combine with great heat evolution or even explosion. Cerium and magnesium mix with absorption of heat. Investigations with tin and lead did not give good results.

Vogel [2] has studied the cerium-lead as well as the cerium-tin alloys. Adding cerium to molten lead a solid homogeneous vitreous alloy is obtained. According to Vogel, cerium behaves with lead as with tin, so that the two equilibrium diagrams have points of similarity. Further, both the cerium-lead and the cerium-tin alloys are formed with energetic evolution of heat, giving rise to several compounds whose melting points are higher than those of their components, and which are decomposed by water with the evolution of gas. The fusion diagram for the cerium-lead alloys has, however, not yet been published.

Lead and tin do not form compounds; the thermal investigation of the system made by Rosenhain and Tukes [3] shows the existence of solid solutions between limits.

Compounds of the Elements of Group V. with each other.

Nitrogen, phosphorus, arsenic, antimony form a natural group; metallic characters are, however, only displayed to a marked extent by antimony and bismuth. By reason of

[1] *Ann. Chem.*, **331**, 46 (1904).
[2] *Zeit. anorg. Chem.*, **72**, 320 (1911).
[3] *Phil. Trans.*, **209** (1908).

their affinities, phosphides and arsenides are grouped apart, together with selenides, tellurides and sulphides.

Antimony and bismuth do not combine chemically, but form an almost complete series of solid solutions.[1]

The reciprocal behaviour of vanadium, niobium and tungsten is not as yet known.

Compounds of the Elements of Group VI. with each other.

Nothing is known of the reciprocal behaviour of chromium, tungsten and uranium. The selenides, tellurides and sulphides are dealt with together with the phosphides and arsenides. The compounds formed by selenium, tellurium and sulphur with the metals of this group do not display true metallic characters.

Compounds of the Elements of Group VII. with each other.

The only metallic element known in this group is manganese; the other elements are, of course, the halogens. Among these, notable exceptions occur to Tammann's first rule. Chlorine and iodine, indeed, form two compounds, ICl and ICl_3[2], while bromine and iodine form the compound BrI.[3]

As these compounds do not show metallic characters it will not be necessary to give any data as to their respective systems.

Compounds of the Elements of Group VIII. with each other.

This group comprises three sub-groups: (1) iron, cobalt, nickel; (2) ruthenium, rhodium, palladium; (3) osmium, iridium, platinum.

[1] *Cf.* Gautier, *Contrib. à l'Étude des Alliages*, p. 114 (1901), Paris. Charpy, *ibid.*, p. 138. Huttner and Tammann, *Zeit. anorg. Chem.*, **44**, 131 (1905). Parravano and Viviani, *Gazz. Chim. Ital.*, **40**, II., 446 (1910).

[2] The equilibrium diagram has been described by Stortenbecker, *Zeit. phys. Chem.*, **3**, 11 (1889).

[3] *Cf.* Meerum-Terwogt, *Zeit. anorg. Chem.*, **47**, 203 (1905).

Iron, cobalt, and nickel mix in the liquid state with other metals in all proportions, with the exception of tin. If a gap in miscibility occurs in one case it occurs also in the other two. Such lack of miscibility decreases from iron to nickel. In the solid state, although these metals generally behave as in the liquid state, there are exceptions. For cobalt, according to Levkonja,[1] Tammann's rule holds, namely, that a metal with a higher melting point can dissolve a greater quantity of a metal with a lower melting point than can the metal with lower melting point of the metal with higher melting point. Tammann's rule for the elements of a natural group also holds for the iron group. If iron does not form a compound with other elements, neither do cobalt and nickel. This rule has been verified in forty-five cases ; the single exception is given by the compound which nickel forms with bismuth. Of the forty-five compounds known, the greatest number, nineteen, is given by nickel ; cobalt gives thirteen and iron eight. The most common formula is AB_3 then AB_2 and A_2B_3.

According to the Periodic System iron, cobalt and nickel should each form a group, (1) with ruthenium and osmium ; (2) with rhodium and iridium ; and (3) with palladium and platinum. Levkonja (*loc. cit.*) maintains that his researches would appear to give support to the proposal made by Biltz [2] to reunite iron, cobalt and nickel in a single natural group.

Compounds of Iron.

Iron-cobalt.—This system was examined by Ruer and Kaneko.[3] Two series of mixed crystals occur (see Fig. 48), one from 0 to 83 per cent. of iron—cobalt β, and the other from 83 to 100 per cent. iron—iron γ. The transformation of cobalt β into cobalt α, though occurring along a continuous curve from 30 to 83 per cent. shows a maximum correspond-

[1] *Zeit. anorg. Chem.*, **59**, 339 (1908).
[2] *Ber.*, **35**, 562 (1902).
[3] *Ferrum*, **11**, 33 (1913).

ing to the compound Fe_4Co_3. Alloys belonging to this curve exhibit magnetic properties. In the mixed crystals between 30 and 83 per cent. of iron the molecules of cobalt and iron unite with the compound, which forms mixed crystals with excess of the constituents. Below 30 per cent. the crystals of Co β change into crystals of Co α (ferromagnetic). Above 83 per cent., crystals of Fe β are formed from Fe γ and crystals of Fe α (strongly magnetic) from Fe β.

Iron-nickel.—This system was studied by Guertler and Tammann [1] and by Ruer and Schüz.[2]

At about 1465° and 66 per cent. of nickel the compound

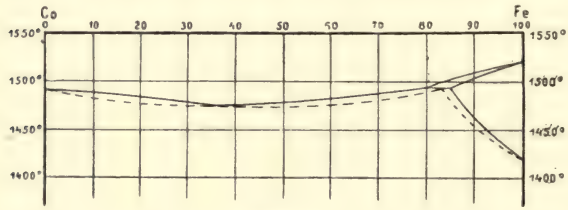

FIG. 48.

$FeNi_2$ occurs. The mixed crystals in equilibrium with the melt on the first branch of the curve should be considered as mixtures of the compound $FeNi_2$ with nickel and iron in excess, while the crystals on the second branch are to be considered as iron γ in which nickel is dissolved. These two series of mixed crystals are sharply distinguished from the crystallographic point of view ; those from 0 to 35 per cent. nickel are isomorphous with iron γ while those from 35 to 100 per cent. nickel are isomorphous with the form of nickel stable at high temperatures and with the compound $FeNi_2$. On cooling the two series of crystals stable at high temperatures, transformations occur into other species of crystals. It appears from the study of these alloys that one of the pro-

[1] *Zeit. anorg. Chem.*, **45**, 211 (1905).
[2] *Metall.*, **7**, 415 (1910).

perties which changes with greatest intensity in these transformations is the magnetic permeability.

Compounds of the Metals of Group I. with Metals of other Groups.

Compounds of Lithium.

The behaviour of lithium with beryllium, calcium, strontium and barium is not known ; with magnesium there is no combination, nor is it known whether lithium reacts with zinc.

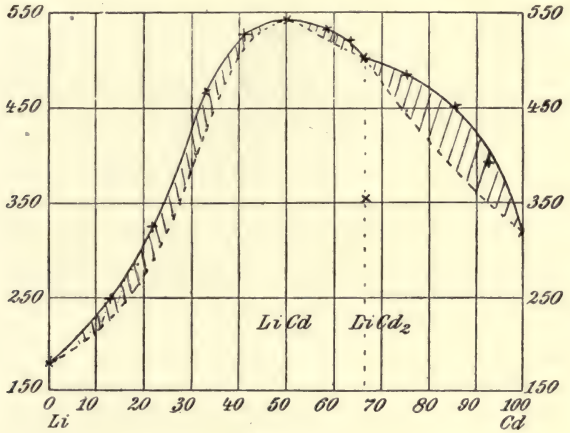

Fig. 49.

Lithium-cadmium.—Lithium forms two compounds with cadmium, LiCd and $LiCd_2$. The system was studied by Masing and Tammann,[1] and is shown in Fig. 49. Lithium and cadmium form an uninterrupted series of mixed crystals with a maximum at 50 per cent. of cadmium. The temperatures at which crystallisation begins can be taken with exactness in all cases, but similar precision is not obtainable for the completion of crystallisation. As Ruer[2] has

[1] *Zeit. anorg. Chem.*, **67**, 183 (1910).
[2] *Zeit. phys. Chem.*, **59**, 16 (1907).

observed, there is at 67·7 per cent. cadmium, in place of an interval of crystallisation a marked arrest, and the alloy crystallises at constant temperature. A small arrest at 356° is noted on the cooling curve of this alloy. The alloy with 67·7 per cent. of cadmium, in addition to showing an arrest, has also a sharp transformation point ; it can be considered to be the compound $LiCd_2$. At 50 per cent. of cadmium,

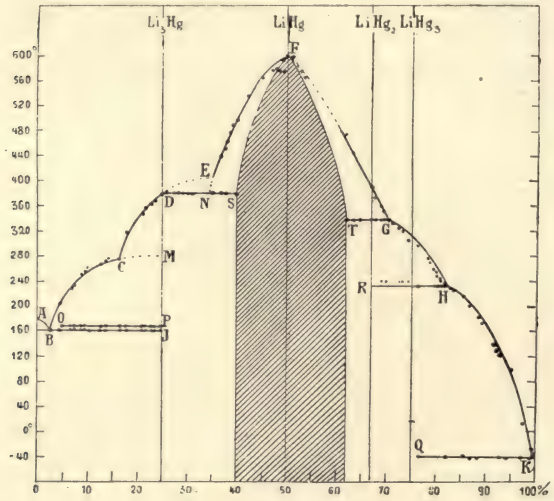

FIG. 50.

corresponding to the maximum of the curve, another arrest point is observed which probably indicates the compound LiCd.

The alloys obtained present a homogeneous appearance ; only the alloy with 92 per cent. of cadmium shows a polyhedric structure when treated with dilute hydrochloric acid. Alloys containing from 100 to 70 per cent. cadmium are stable in the air ; with increase in the lithium content their oxidisability increases ; thus the alloys with more than 50

per cent. lithium become red, those with 13 per cent. of cadmium dark brown, and those with still less of this metal black.

Lithium-mercury.—Lithium forms the following compounds with mercury: Li_3Hg, Li_2Hg, LiHg, $LiHg_2$ and $LiHg_3$.

The equilibrium diagram of the lithium amalgams is shown in Fig. 50 and has been traced by G. Zukovski.[1] Kerp, Böttger, Winter and Iggena,[2] studying the amalgams of the alkali and alkaline earth metals had already obtained a compound $LiHg_5$. Guntz and Férée [3] admit the existence of this latter compound. Maey,[4] from a study of the variations of specific volume with composition, established the existence of the compounds $LiHg_5$, $LiHg_3$, LiHg and Li_3Hg.

In the diagram traced by Zukovski the maximum point of the system is at 50 per cent. mercury, corresponding to a compound LiHg. The cooling curve shows other arrests from 2·4 to 24·8 per cent. mercury, corresponding to the compound Li_5Hg. *C* represents a new compound which decomposes on melting. The transformation point *G* indicates a new solid phase of the composition $LiHg_2$. (The existence of this compound was confirmed by calorimetric measurements.) The point *H* represents the compound $LiHg_3$. In the rest of the curve no other arrest points are noted, which contradicts the contention of other workers as to the occurrence of a compound $LiHg_5$. The compound LiHg separates in needle-shaped crystals.

Lithium-tin.—Lithium combines with tin forming the following compounds:—

$$Li_2Sn_5,\ Li_3Sn_2 \text{ and } Li_4Sn.$$

The diagram has been worked out by Masing and Tammann [5] and is shown in Fig. 51. Adding lithium to tin, the

[1] *Zeit. anorg. Chem.*, **71**, 403 (1911).
[2] *Ibid.*, **25**, 16 (1900).
[3] *Bull. Soc. Chim.*, **15**, 834 (1896).
[4] *Zeit. phys. Chem.*, **29**, 119 (1898).
[5] *Zeit. anorg. Chem.*, **67**, 183 (1910).

melting point of the latter is lowered until the eutectic point b is reached, corresponding to about 95 per cent. of tin. The cooling curve of the alloy of this composition shows an arrest at 214°, and the structure of the solid alloy is eutectic. Adding more lithium, the liquidus curve rises along the branch b c. The compound Li_2Sn_5 first separates at 320° and 72 per cent. of tin in the form of white crystals, sur-

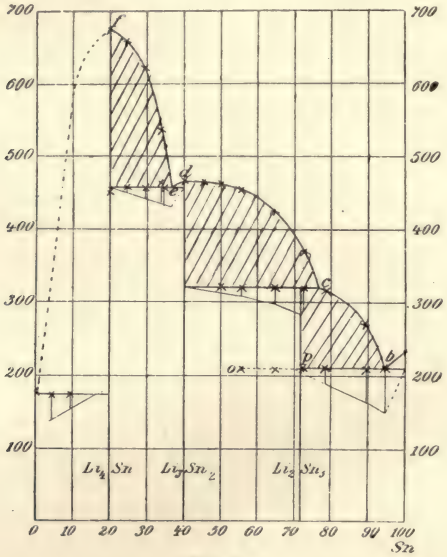

FIG. 51.

rounded by the eutectic, which slowly become yellow when exposed to the air. At 465° and 40 per cent. tin a slackening is shown which corresponds to the compound Li_3Sn_2. The reaction between Li_3Sn_2 and the melt c does not take place completely, for the eutectic horizontal b o extends beyond the point p, which corresponds to the composition of Li_2Sn_5. In consequence, alloys containing less than 77 per cent. of tin are composed of three species of crystals; the crystals

Li_3Sn_2 are surrounded by Li_2Sn_5, and among the latter is found the eutectic *b*, containing tin. The crystals of Li_3Sn_2 are long, and on exposure to air become first yellow and then brown. From *e* the curve rises rapidly to the maximum *f* at 20 per cent. of tin, which probably corresponds to the compound Li_4Sn. The crystals at this point have a

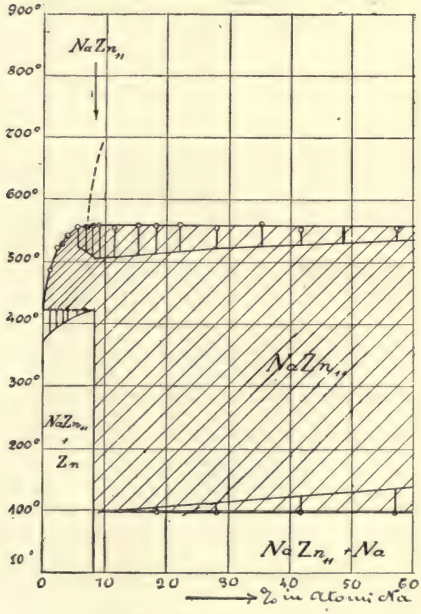

FIG. 52.

micaceous structure and are very brittle; they acquire a dark blue colour on exposure.

COMPOUNDS OF SODIUM.

Sodium-magnesium.—Sodium forms no compound with magnesium. The system was investigated by Mathewson.[1]

Sodium-zinc.—With zinc, sodium forms the compound

[1] *Zeit. anorg. Chem.*, **48**, 193 (1906).

$NaZn_{11}$ or $NaZn_{12}$. The equilibrium diagram, due to Mathewson (*loc. cit.*), is shown in Fig. 52. The two metals are only slightly soluble in each other even at high temperatures. At 557°, zinc dissolves about 6 per cent. of sodium, while sodium scarcely dissolves zinc at all. However, at

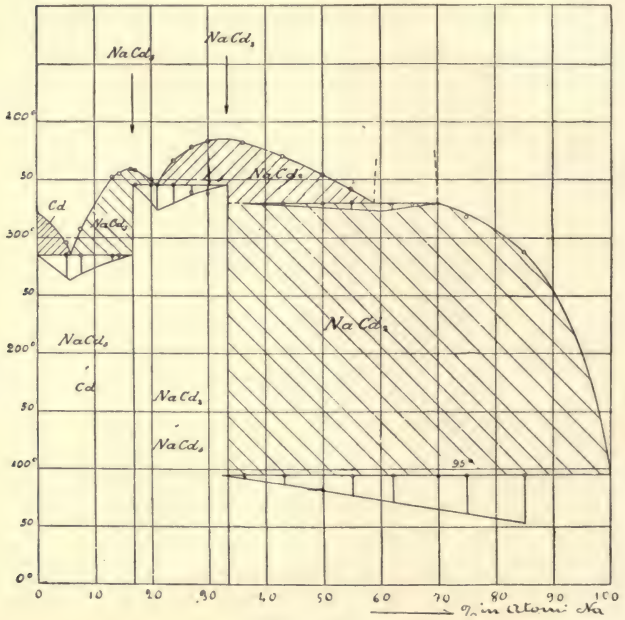

FIG. 53.

about this temperature and at a concentration of 8·36 per cent. of sodium a compound is formed of uncertain formula, for while the diagram suggests $NaZn_{11}$ as most probable, analyses of the lower strata of certain melts give $NaZn_{12}$. On melting, the compound gives a liquid richer in zinc together with almost pure sodium.

The compound is harder and more brittle than zinc, and

on exposure to air is slowly covered with a white layer of zinc hydroxide.

Sodium-cadmium.—With cadmium, sodium forms the two compounds $NaCd_5$ and $NaCd_2$. Fig. 53 gives the equilibrium diagram of this system, studied first by Kurnakoff,[1] then by Mathewson,[2] and finally by Kurnakoff and Kusnetzoff.[3] The diagram shown is due to Mathewson, who has established, both by means of thermal analysis and also directly by removing the liquid in a pipette, the gap in solubility which occurs from 30 to 40 per cent. of cadmium. Two maxima are observed corresponding to the two compounds, for $NaCd_5$ at 360° and 16·4 per cent. sodium, and for $NaCd_2$ at 382° and 33·06 per cent. of sodium. According to Kurnakoff, in the place of $NaCd_5$, $NaCd_6$ is formed. Mathewson does not report the occurrence of mixed crystals; Kurnakoff, on the other hand, states that $NaCd_6$ can dissolve a certain quantity of $NaCd_2$ in solid solution.

The compound $NaCd_2$ is shining and brittle. The alloys of the compound $NaCd_5$ and the eutectic are harder and show a finer structure than the compound $NaCd_2$. The alloys of the compound $NaCd_5$ and the eutectic with 16 per cent. of sodium can be cut with a knife. The compounds are harder than cadmium; $NaCd_5$ is as hard as calc spar, and $NaCd_2$ is a little harder.

In moist air both compounds are oxidised, $NaCd_2$ more rapidly than $NaCd_5$.

Sodium-mercury.—The sodium amalgams are very diverse and include compounds of the following formulæ:—Na_3Hg, Na_5Hg_2, Na_3Hg_2, NaHg, Na_7Hg_8, $NaHg_2$ and $NaHg_4$.

The system was studied thermally by Schüller,[4] who reports the existence of a compound $Na_{12}Hg_{13}$, while E. Vanstone[5] from a study of the specific volumes of the

[1] *Zeit. anorg. Chem.*, **23**, 439 (1900).
[2] *Ibid.*, **50**, 180 (1906).
[3] *Ibid.*, **52**, 173 (1907).
[4] *Ibid.*, **40**, 385 (1904).
[5] *Chem. News*, **103**, 181, 198, 207 (1911).

system *sodium-mercury* believes the existence of a compound Na_7Hg_8 more probable.

Fig. 54 shows the equilibrium diagram for sodium-mercury. The compound NaHg is formed at 50 per cent. sodium and 219°, with such strong super-cooling, however, that the corre-

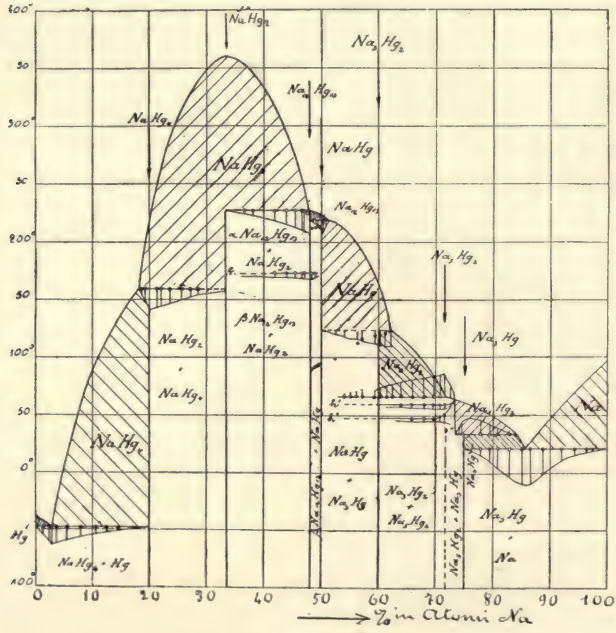

FIG. 54.

sponding arrest points are not found on the horizontal as would be expected. An imperfect equilibrium is established, and hence the arrest points at 123° show a quantity of sodium less than 50 per cent. At 61 per cent. of sodium and 125° the compound Na_3Hg_2 is probably formed; in this region, also, super-cooling is observed. $Na_{12}Hg_{13}$ is shown by a discontinuity at 227° and 48 per cent. of sodium. But, as

has already been said, the formula of this compound is uncertain. The formulæ attributed to the other compounds may be considered reliable. Mixed crystals are formed among the compounds.

Sodium-aluminium.—Sodium forms no compounds with

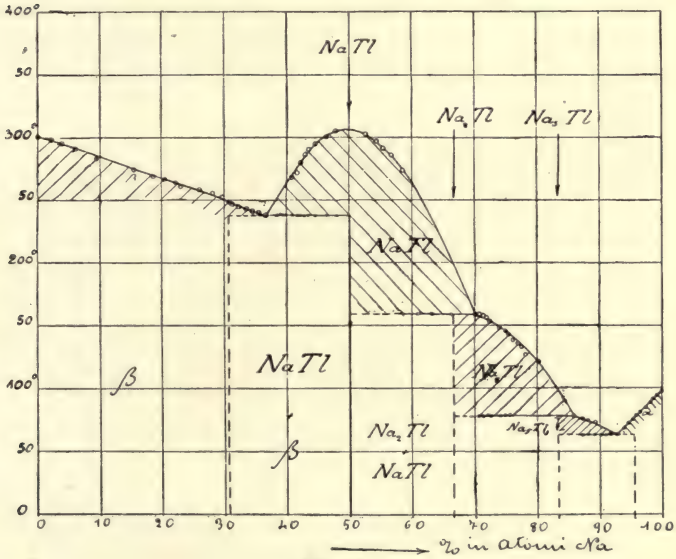

FIG. 55.

aluminium. The system has been studied by Mathewson [1] and Smith.[2]

Sodium-thallium.—This system was studied by Kurnakoff and Pushin,[3] who have established the existence of the compound NaTl, which agrees with the monovalency of thallium. The diagram shown in Fig. 55 indicates the existence of two other compounds which separate respectively at 158° and 33 per cent. thallium and 77·9° and 17·2 per cent. thallium ;

[1] *Zeit. anorg. Chem.*, **48**, 192 (1906).
[2] *Ibid.*, **56**, 112 (1907).
[3] *Ibid.*, **30**, 87 (1902).

it is doubtful, however, if the formulæ Na_2Tl and Na_5Tl attributed to them are reliable. NaTl crystallises in three-rayed arboriform growths, and is formed with considerable development of heat. The melting point of this compound is 305·8°, or somewhat higher than that of pure thallium. The compound is harder and more brittle than its components.

Sodium-tin.—Sodium forms the following compounds with

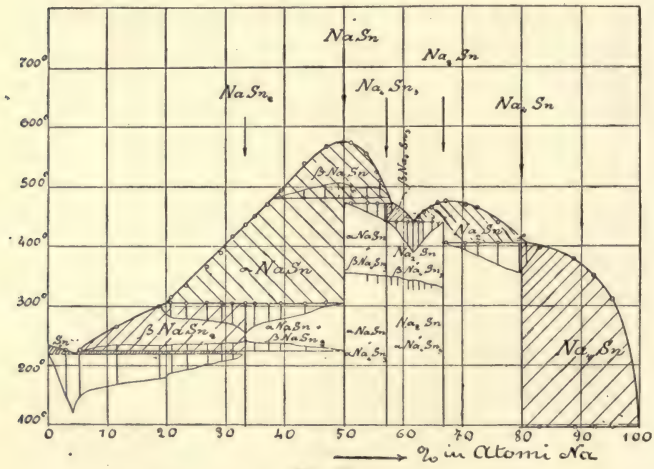

FIG. 56.

tin : Na_4Sn, Na_2Sn, Na_4Sn_3, NaSn and $NaSn_2$. The system has been worked out by Mathewson,[1] and its diagram is shown in Fig. 56. The fusion curve shows two distinct maxima. The compound in equilibrium with the melt at 405° and at a concentration of 80 per cent. sodium has the formula Na_4Sn. At 405° it decomposes to a melt of composition indicated by *B* and the compound Na_2Sn. The latter compound corresponds to the maximum at 66·9 per cent. sodium and 477°, while Na_4Sn_3 occurs at 57 per cent.

[1] *Zeit. anorg. Chem.*, **46**, 94 (1905).

of sodium. At 478° the latter decomposes, forming crystals of the compound NaSn, which is found at the maximum point at a concentration of 50 per cent. of sodium. At 483° a polymorphic transformation takes place. Finally $NaSn_2$ is found at 33·5 per cent. sodium. When warmed it decom-

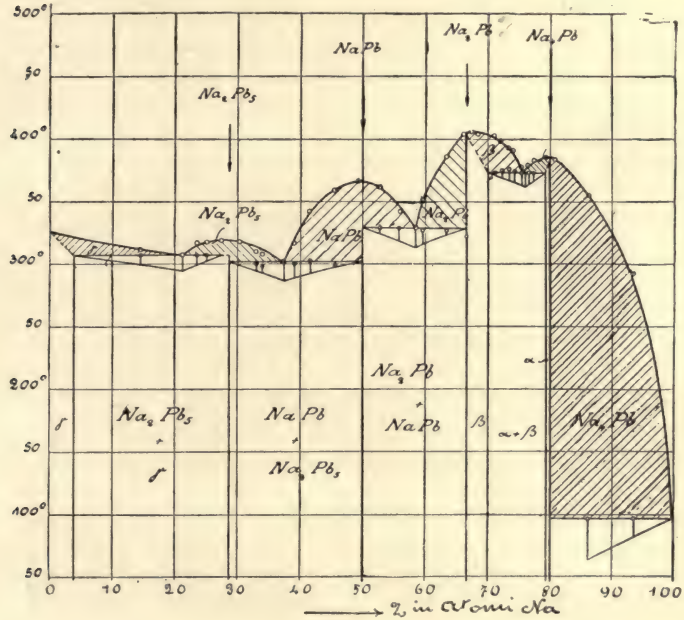

FIG. 57.

poses at 305° into crystals of the compound NaSn and a melt containing about 20 per cent. sodium.

Freshly cut, $NaSn_2$ has a steel blue colour; Na_4Sn_3 has a pale blue colour; the other compounds are similar in colour either to sodium or to tin.

The compound Na_4Sn_3 is fairly hard and brittle; the other compounds are more brittle. The latent heats of fusion have been calculated approximately from the

thermometric arrests by Tammann's method; the values obtained are as follows: $Na_4Sn = 11$; $Na_2Sn = 12$; $Na_4Sn_3 = 11$; Na_4Sn_3 (transformation) $= 4$; $NaSn = 14$; NaSn (transformation) $= 7$; $NaSn_2 = 9$; $NaSn_2$ (transformation) $= 4$.

Sodium-lead. — This system was studied by Kurnakoff,[1]

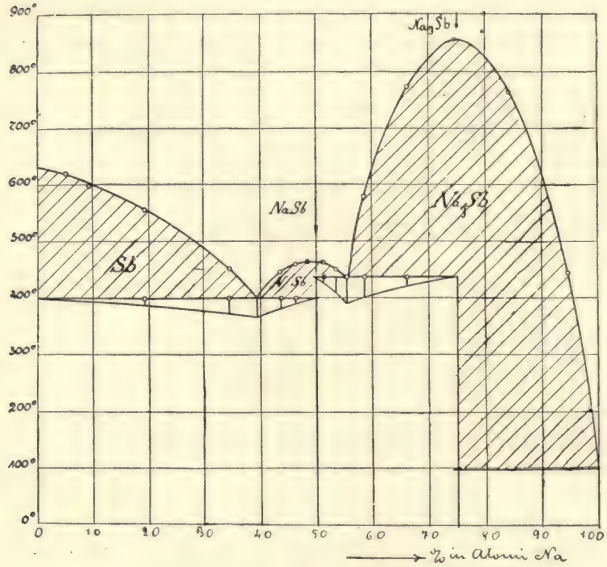

FIG. 58.

and later by Mathewson,[2] who have noted the occurrence of the following compounds :—

Na_4Pb, Na_2Pb, NaPb and Na_2Pb_5. The curve of fusion is shown in Fig. 57 taken from Mathewson's paper and exhibits four maxima, the first at 386° and 80 per cent. sodium, the second at 405° and 67·2 per cent. sodium, the

[1] *Zeit. anorg. Chem.*, **23**, 439 (1900).
[2] *Ibid.*, **50**, 172 (1906).

third at 367° and 49·6 per cent. sodium, and the last at 319° and 28·2 per cent. sodium. Some doubt, however, exists about the compound Na_2Pb_5, which might be replaced by the compound $NaPb_3$. Mathewson, however, decides for Na_2Pb_5, seeing that while its melt shows a sharp arrest point, that of the second only gives a discontinuity.

Two of the compounds, Na_2Pb and Na_4Pb, form mixed crystals with each other. The alloys of this series oxidise easily—those with high sodium content more easily than those with low content of this metal. As to hardness, NaPb and Na_2Pb_5 are almost as hard as calc spar, while Na_4Pb and Na_2Pb are rather less hard. Na_2Pb has a light blue colour, while NaPb is light grey.

Sodium-antimony.—Sodium combines with antimony, forming the two compounds Na_3Sb and NaSb. Fig. 58, taken from Mathewson,[1] is the fusion diagram. Two maxima are shown, one at 856° and about 75 per cent. sodium, corresponding to the first compound, and the other at 465° and 50 per cent. sodium, corresponding to the second compound. NaSb is almost as hard as gypsum and is of the same colour as antimony, while Na_3Sb is deep blue and somewhat harder. The sodium-antimony alloys ignite spontaneously in the air.

Sodium-bismuth.—This system has been investigated by Kurnakoff[2] and Mathewson.[3] The diagram (Fig. 59) shows the existence of the two compounds Na_3Bi and NaBi. The first is indicated by a distinct maximum at 775° and 75·15 per cent. sodium, the second is represented by a break and is formed at 445° and about 49 per cent. of sodium. Here also, as in the case of NaSb, the two metals develop heat strongly on being melted together. Na_3Bi has a violet blue colour when freshly cut; pieces larger than 10 grams inflame spontaneously in the air on slight heating. The hardness

[1] *Zeit. anorg. Chem.*, **56**, 192 (1906).
[2] *Ibid.*, **23**, 439 (1900).
[3] *Ibid.*, **50**, 187 (1906).

of the two compounds is almost equal to that of bismuth and of calc spar.

Potassium Compounds.

Potassium-zinc.—Potassium forms a compound with zinc whose probable formula is KZn_{11} or KZn_{12}. The system was

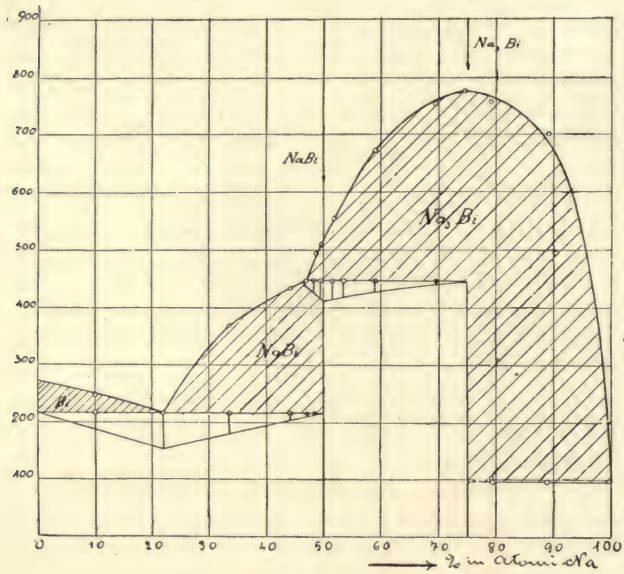

Fig. 59.

studied by Smith.[1] As Fig. 60 shows, the two metals have a very small reciprocal solubility at 600°, since at that temperature most melts consist of two liquid strata. At 585° a metastable form of the compound separates, passing into the stable form when the solidification is scarcely complete. Between 405° and 510°, from 9 to 40 per cent. potassium, thermal effects are indicated. The horizontal at 510° marks

[1] *Zeit. anorg. Chem.*, **56**, 113 (1907).

a transformation of the compound KZn_{12}. The structure of the alloys is finely granular. They are easily altered in the air.

Potassium-cadmium.—Potassium combines with cadmium, forming the compounds KCd_{12} and KCd_7. Fig. 61, taken from Smith [1] is the fusion diagram. The mutual solubility

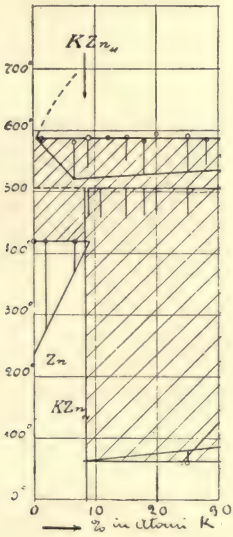

FIG. 60.

of the metals is small. At 468° there is a gap of solubility between 17 and 99 per cent. potassium. At 473° and 12·5 per cent. potassium, KCd_7 separates and at about 485° and 7 per cent. potassium, KCd_{12}. The formula given to the latter is, however, not perfectly reliable ; KCd_{11} might be substituted for it.

These alloys oxidise easily in air.

Potassium-mercury.—The potassium amalgams, like those

[1] *Zeit. anorg. Chem.*, **56**, 113 (1907).

of sodium, are numerous. Kurnakoff[1] first studied the system and his data were later confirmed by Jänecke.[2] The compounds probably formed are KHg, KHg_2, KHg_3, K_2Hg_9, and KHg_9, all of which Kurnakoff admits with the exception of K_2Hg_9 whose formula he believes to be KHg_5.

Fig. 62 gives the fusion diagram. The compound KHg, which melts at 178°, is shown by a discontinuity in the curve; the compound KHg_2 alone shows a maximum, which occurs

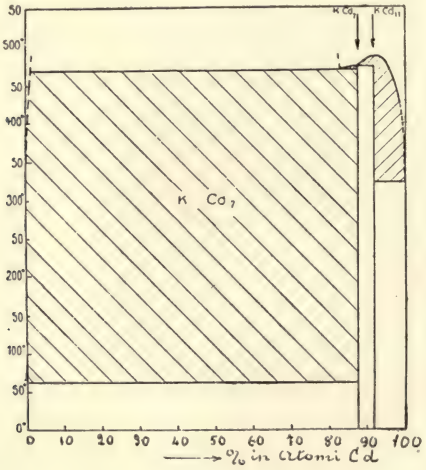

FIG. 61.

at 279° and about 65 per cent. of mercury. The other compounds are formed in a limited concentration interval. KHg_3 occurs at 204° and 78 per cent. mercury, K_2Hg_9 at 173° and about 83 per cent. mercury, and KHg_9 at 70° and 90 per cent. of mercury. The homogeneity of the last three, on which some doubt might be cast, is shown by microscopic analysis, for the first crystallises in rods about one centi-

[1] *Zeit. anorg. Chem.*, **23**, 439 (1900).
[2] *Zeit. phys. Chem.*, **58**, 245 (1907).

metre long, the second in hexagonal plates, and the third in regular, mainly cubic form.

Potassium-thallium.—As noted by Kurnakoff and Pushin,[1] potassium forms with thallium the compounds KTl and K_2Tl.

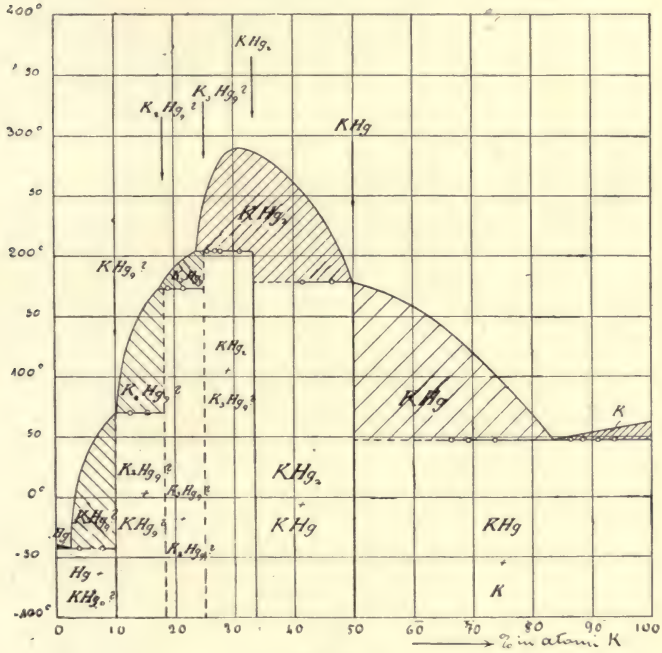

FIG. 62.

The equilibrium curve is shown in Fig. 63. The existence of the second compound has been established by analogy with the behaviour of sodium with thallium, since the discontinuity which is found at 242° and 32·9 per cent. is not very pronounced. At 335°, the curve shows a maximum, corresponding to KTl. The melting point of this compound

[1] *Zeit. anorg. Chem.*, **30**, 87 (1902).

is, as may be seen from the diagram, somewhat higher than that of pure thallium. The compound KTl crystallises in compact brittle cubes, which react with moist air. It is formed with considerable evolution of heat.

Potassium-tin.—Potassium forms with tin numerous compounds, from which, however, K_4Sn, corresponding to the saline valency of tin, is lacking, although a corresponding

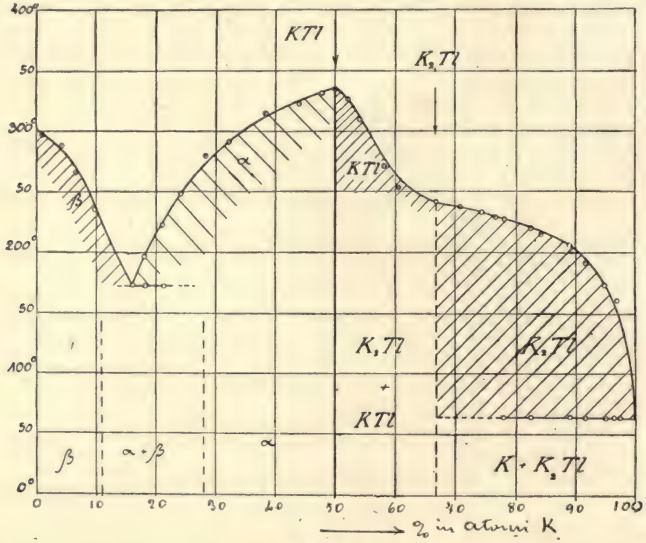

FIG. 63.

sodium compound occurs, Na_4Sn. The following are the potassium-tin compounds: KSn_4, KSn_2, KSn and K_2Sn. Fig. 64 indicates the diagram of the system which was studied by Smith.[1] The melting points of the alloys are, over a certain range, above the boiling point of pure potassium (757°). KSn_4 separates at 600° and 20 per cent. potassium from the melt and from a compound of uncertain formula, possibly KSn_2, formed at a higher temperature. At above

[1] *Zeit. anorg. Chem.*, **56**, 129 (1907).

600° and 50 per cent., KSn is formed which, reacting with the melt, gives the compound K_2Sn (?) with a maximal arrest at 535°.

Potassium-lead.—Smith[1] has also studied this system in which the compounds KPb_4, KPb_2 and K_2Pb are formed as indicated in Fig. 65. In this series the type K_4Pb, which occurs in the sodium-lead system and corresponds to a saline

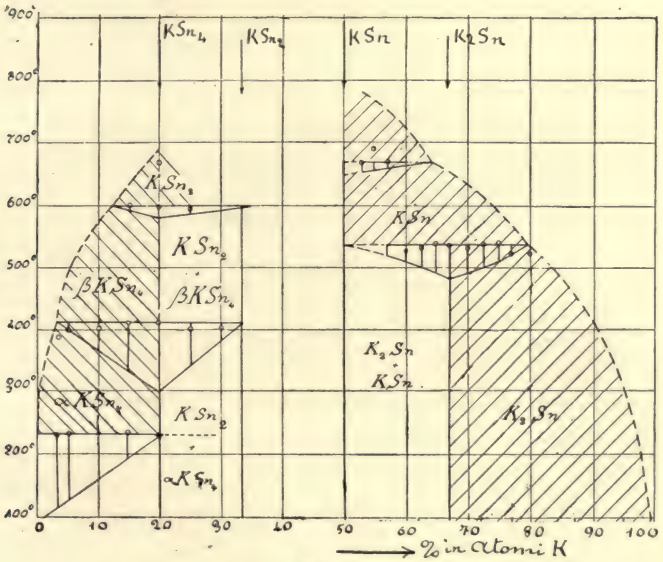

FIG. 64.

valency of lead, is missing. At 568°, between 35 and 75 per cent. of potassium, a compound crystallises out from the two liquid strata to which the formula K_2Pb is given. At 380° a transformation occurs, probably into another form of the compound. At 337° and 33·33 per cent. potassium, KPb_2 is formed, while at 295° there separates from the crystals of this compound, and from the melt, KPb_4, whose formula is not, however, well established. It is, further, uncertain

[1] *Loc. cit.*

whether the eutectic horizontal at 376° consists of two horizontals, of which one corresponds to a compound X between K_2Pb and KPb_2. Smith did not observe an eutectic point between K and K_2Pb; yet the alloys between 65 and 98 per cent. potassium show a point of arrest 4° to 6° lower than the melting point of potassium.

Potassium-antimony.—Although we have no very exten-

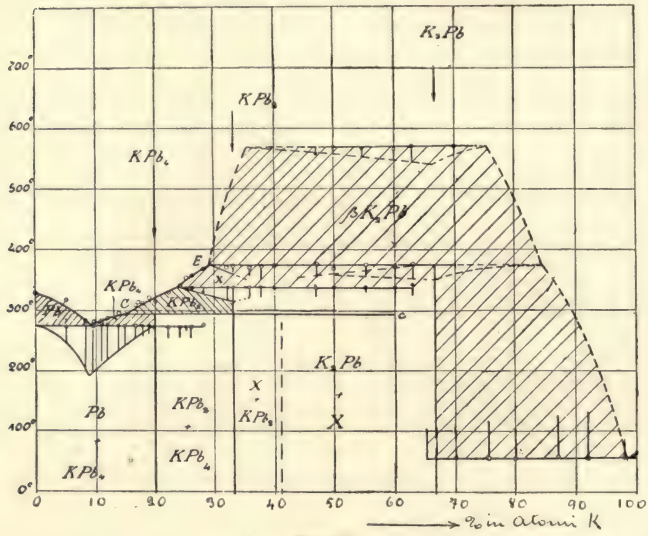

FIG. 65.

sive knowledge of the compounds between potassium and antimony, it is well established that the two elements do combine. The system potassium-antimony has recently been studied by Parravano.[1] The diagram is shown in Fig. 66. It will be seen that the curve is quite simple and shows the existence of the two compounds K_3Sb and KSb, having melting points at 812° and 605° respectively. The formation of these compounds is attended with a consider-

[1] *Gazz. Chim. Ital.*, I., 485 (1915).

able evolution of heat. The compound K_3Sb, in which the trivalency of antimony is shown, has a yellowish-green colour and alters rapidly in the air ; the compound KSb crystallises in long slender prisms of a colour similar to antimony and is less rapidly attacked by air than the former compound.

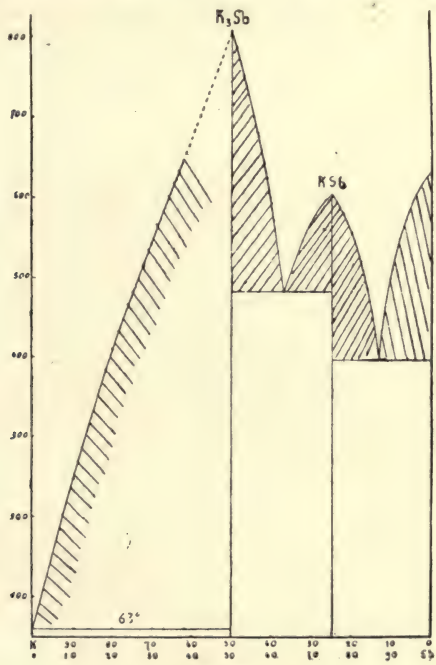

FIG. 66.

Potassium-bismuth.—Potassium combines with bismuth, according to Smith [1] to form a rather numerous series of compounds. They comprise KBi_2, K_9Bi_7 (?), K_3Bi_2 and K_3Bi.

Fig. 67 is the diagram for this system. K_3Bi gives a maximum at 75 per cent. of potassium and 671°. At 286°, arrest points occur between 60 and 83 per cent. of potassium,

[1] *Zeit. anorg. Chem.*, **56**, 125 (1907).

with a maximum at 75 per cent. These probably indicate a transformation of α K_3Bi into β K_3Bi a companied by an increase in volume. Further, at 420° with a maximal arrest at 60 per cent. potassium, a compound, probably K_3Bi_2, separates. From these crystals and the melt at 54 per cent., another compound separates at 373°, also of uncertain formula, K_9Bi_7. Another maximum occurs on the curve at

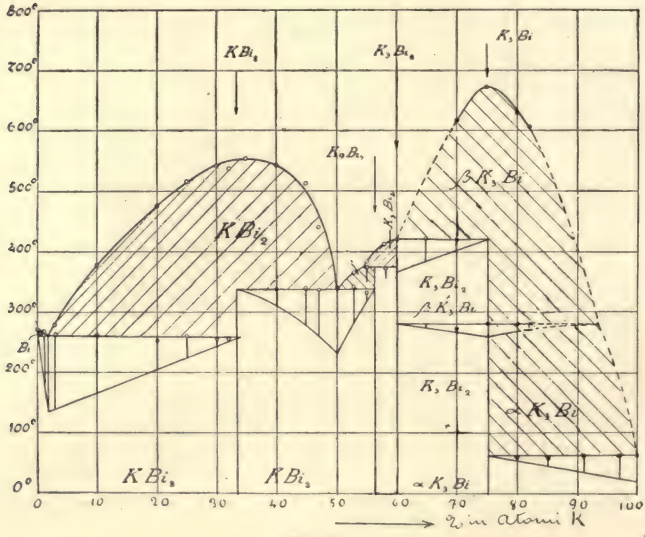

FIG. 67.

about 550° and 33·33 per cent. of potassium, due to a compound whose formula can safely be taken as KBi_2.

The two metals develop a considerable amount of heat on being melted together, due, it is maintained, to the formation of K_3Bi.

RUBIDIUM COMPOUNDS.

Rubidium-mercury.—Little is at present known of the compounds of rubidium with other metals. The system

rubidium-mercury has been studied by Kurnakoff and Zukovsky,[1] but only over a limited range of concentration. The existence of a compound $RbHg_6$ was noted, which melted at 136·5° with decomposition. At 70·2° there is a transformation point, and here a compound richer in mercury begins to separate, to which, by analogy with the corresponding cæsium compound, the formula $RbHg_{10}$ may be given.

Cæsium Compounds.

Cæsium-mercury.—Our information on the metallic compounds of cæsium is also very scanty. The compounds with mercury are well known. The system *cæsium-mercury* studied by Kurnakoff and Zukovsky (*loc. cit.*) is shown in Fig. 68. The following compounds are formed: $CsHg_{10}$, $CsHg_6$, $CsHg_4$, $CsHg_2$, CsHg and Cs_2Hg.

Three maxima are seen in the diagram representing the three compounds $CsHg_2$, $CsHg_4$ and $CsHg_6$ respectively. They occur at 208·2° and 67 per cent. mercury, 163·5° and 80 per cent. mercury and 157·7° and 86 per cent. mercury, and melt without decomposition. At 188° weak arrests are noted between 62·4 and 65·8 per cent. mercury, which probably imply a polymorphic transformation of the compound $CsHg_2$. The formation of solid solutions is observed on the curve. At 13·1° and 91 per cent. mercury, the compound $CsHg_6$ is transformed into $CsHg_{10}$; this formula is, however, not well established. Other arrest points occur at 50 per cent. and at 37 per cent. of mercury (CsHg and $CsHg_2$), but as to these compounds there is considerable uncertainty.

Copper Compounds.

Copper-beryllium.—Little is known of the beryllium alloys. The alloys with copper have only been studied by Lebeau[2] and, more recently, by G. Oesterheld,[3] who studied the system

[1] *Zeit. anorg. Chem.*, **52**, 416 (1907).

[2] *C. R.*, **125**, 1172 (1897). *Bull. Soc. Chem.*, (3), **19**, 64 (1898). *Ann. Chim. Phys.*, (7), **16**, 498 (1899).

[3] *Zeit. anorg. Chem.*, **97**, 6 (1916).

over a limited range. The compound $CuBe_3$ occurs. The melting point of copper is lowered until a concentration of 10 per cent. beryllium is reached, and the lowering is accompanied by the formation of solid solutions. Beyond this

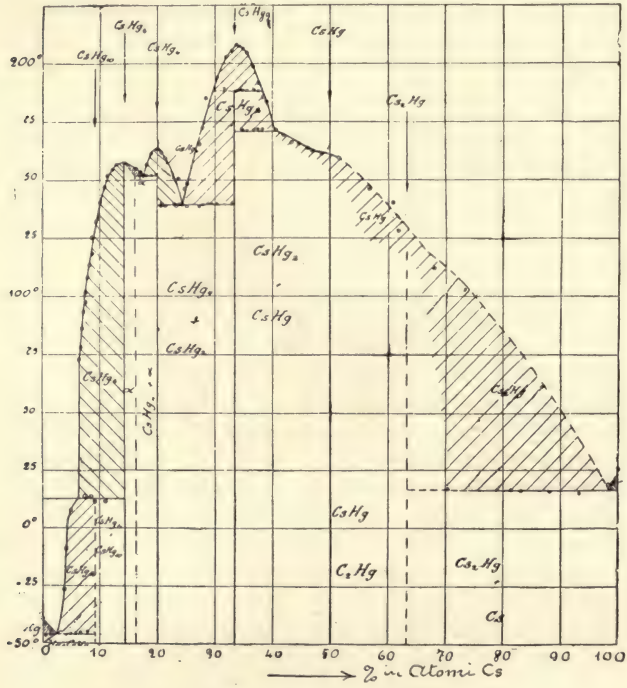

FIG. 68.

limit for a short interval the solidus and liquidus curves have an unusual form and subsequently pass through a minimum and a point of inflection. At 575° there is an eutectic point for 31 per cent. beryllium, and thence the curve rises to a maximum corresponding to the compound mentioned.

The copper-beryllium alloys can dissolve in nitric acid.

Copper-Magnesium.—Copper forms with magnesium two compounds, namely, $CuMg_2$ and Cu_2Mg. The system has

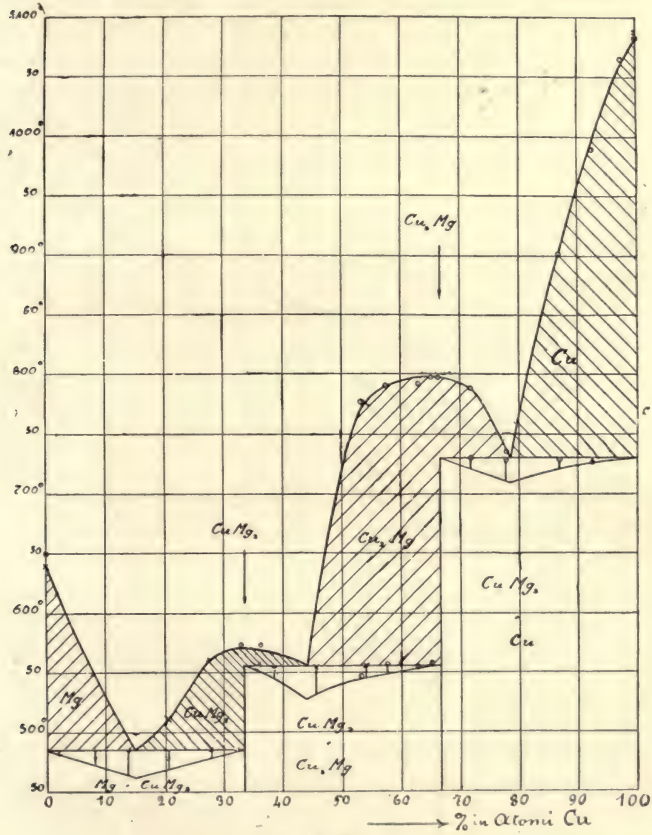

FIG. 69.

been studied by several workers, including Boudouard,[1] Urasoff [2] and Sahmen.[3]

[1] *C. R.*, **135**, 794 (1902).
[2] *Chem. Centr.*, 1908, I., 1038.
[3] *Zeit. anorg. Chem.*, **57**, 26 (1908).

The data obtained by the two latter are quite concordant. As Fig. 69 shows, there are two maxima, one for Cu_2Mg at 33·3 per cent. magnesium and 797°, and the other for $CuMg_2$ at 66·7 per cent. magnesium and 570°. Mixed crystals are lacking in this system. Boudouard also reports a compound CuMg. Sahmen states that the eutectic point between Cu_2Mg and CuMg is found between 55 and 57 per cent. of

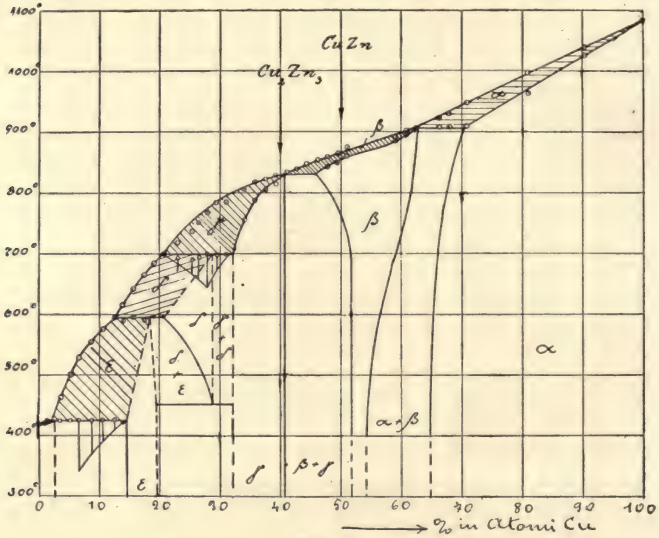

FIG. 70.

magnesium, while according to Urasoff it is found at 58·5 per cent. of magnesium. Both compounds are very brittle and have the colour of pure magnesium. Only those alloys rich in copper which contain a large quantity of that metal in the free state exhibit a red colour.

Copper-zinc.—Copper combines with zinc, forming the two compounds Cu_2Zn_3 and CuZn. The equilibrium diagram of these alloys has been investigated by Roberts-Austen,[1]

[1] *Proc. Inst. Mech. Eng.*, 1897, p. 31.

Shepherd,[1] Tafel,[2] Carpenter and Edwards,[3] and lastly by Parravano.[4] As is seen from the diagram, which epitomises our knowledge of the brass alloys (see Fig. 70), Cu_2Zn_3 separates at 833° and 60 per cent. zinc, and CuZn at 1005° and about 50 per cent. It was noted that the region of existence of this latter compound became more restricted with fall of temperature.

, Shepherd maintains that the curve does not necessitate the unconditional admission that compounds are formed. Bornemann[5] refutes this for various reasons. Above all because the field of existence of homogeneous α crystals enlarges with fall of temperature towards the Zn axis. The solubility of the substance richer in zinc in the solid solution indicated by α increases with fall of temperature. The solution process must be exothermic and an exothermic compound must be formed. To support his contentions, Bornemann cites the work of Backer[6] and Herschkovitch[7] on the heats of formation of the copper-zinc alloys ; for all concentrations the values obtained were positive. Further, allowing the existence of the compound, and this Tafel holds to be certain, as well defined and practically undissociated in the pure state, the micrographic study and the diagram should be in perfect agreement.

To resolve the question, Bornemann examined the methods used to determine the constitution of compounds by observing the relation between concentration and (*a*) electrical conductivity and temperature coefficient of electrical resistance, (*b*) specific gravity and specific volume, (*c*) electrolytic potential, and (*d*) chemical and electrochemical reactivity. In all cases the presence of compounds is distinguished from the presence of mixed crystals, since the

[1] *J. Phys. Chem.*, **3**, 421 (1904).
[2] *Métallurgie*, **5**, 349, 375 (1908).
[3] *Int. Zeit. Metall.*, **2**, 129 (1912).
[4] *Gazz. Chim. Ital.*, **44**, II., 475 (1914).
[5] *Die binaren Metallegierungen*, p. 19, Halle, 1909.
[6] *Zeit. phys. Chem.*, **38**, 630 (1901).
[7] *Ibid.*, **27**, 164 (1898).

formation of the former produces much more marked changes than the latter.

(*a*) Le Chatelier [1] and Guertler [2] with regard to the first method have laid down the following rules : (1) the curve of concentration-electrical conductivity is practically a straight line in all cases where an alloy consists of a heterogeneous mixture of two constituents ; (2) wherever mixed crystals occur the curve shows a marked lowering. The measurements carried out by Matthiessen,[3] Haas,[4] and Weber,[5] show that while the existence of the compound CuZn is probable, other compounds do not exist between this and pure copper. The compound Cu_2Zn_3 may exist although apparently it shows no maximal conductivity.

(*b*) Specific volume should change in a linear manner with concentration in the case of heterogeneous mixtures. In the case of mixed crystals a change from one series to another should be marked by a discontinuity in the curve. If at the point of discontinuity mixed crystals do not exist the new phase is to be taken as a compound. The diagram showing Maey's [6] observations shows no marked discontinuities with the exception of one at 40 per cent. copper, corresponding to the compound Cu_2Zn_3.

(*c*) With regard to electrolytic potential two principles must be noted : (1) where mixed crystals occur the potential should fall in a continuous curve ; (2) in heterogeneous systems of saturated mixed crystals the potential should remain constant. In the case where compounds are present without the formation of mixed crystals, each compound must be reckoned as a single new substance, and the diagram is divided up accordingly into corresponding parts. A compound should be marked by a decided fall of potential. In practice the distinction between mixed crystals and com-

[1] *Rev. Génér. des Sciences*, **6**, 531 (1895).
[2] *Contrib. à l'Etude des Alliages*, Paris, 1901, p. 446.
[3] *Rep. Brit. Ass.*, 1863, 127.
[4] *Wied. Ann.*, **52**, 673 (1894).
[5] *Ibid.*, **68**, 705 (1899).
[6] *Zeit. phys. Chem.*, **38**, 291 and 299 (1901).

pounds is not so simple, since most usually the fall of potential extends over a certain range of concentration and is graphically represented by a curve. Consequently it is necessary to examine also the fusion diagram. Pushin's [1] curve, though showing some errors in measurement, indicates a sharp fall of potential corresponding to 60 per cent. zinc, *i.e.*, to the compound Cu_2Zn_3. Another, though small, fall takes place at about 50 per cent. and may correspond to strongly dissociated CuZn. The other falls of potential given in Pushin's curve are very probably not due to compounds. Sackur,[2] by chemical means, has demonstrated two considerable falls of potential.

(*d*) Sackur,[3] and Lincoln, Klein and Howe [4] have studied the chemical and electro-chemical reactivity of the copper-zinc alloys. The former has determined the solubility of alloys in dilute acids in the presence of air. He observed that there were distinct changes for the crystals β and γ, and these may consequently be compounds. The other authors studied electrolytic reactivity in neutral saline solutions, obtaining hydrates or basic salts which were mechanically removed from the anodes. From their curve it appears that at about 40 per cent. the quantity of copper oxidised is reduced almost to nothing, which is another proof of the existence of the compound Cu_2Zn_3.

Summarising the evidence it may be said that the compound Cu_2Zn_3 certainly exists and can melt without decomposition. A compound CuSn also probably exists which is strongly dissociated at high temperatures and to a marked degree at lower temperatures, giving rise to copper and the compound Cu_2Zn_3, accompanied by the formation of mixed crystals with the components.

Copper-calcium.—Copper is said to combine with calcium, forming the compounds Cu_4Ca and $CuCa_4$. The existence

[1] *Zeit. anorg. Chem.*, **56**, 28 (1907).
[2] *Ber.*, **38**, 2186 (1905).
[3] *Ibid.*, **38**, 2190 (1905).
[4] *J. Phys. Chem.*, **11**, 501 (1907).

of the latter compound is somewhat doubtful, as N. Baar[1] has shown in his study of the system. The diagram is given in Fig. 71. From the eutectic point the curve rises up to 13·7 per cent. by weight of calcium, a maximum corresponding to the compound Cu_4Ca, which melts at 933°. From this point to the next, eutectic crystals of Cu_4Ca separate. From melts containing more than 38 per cent. of calcium, a series of mixed crystals separate whose last member contains

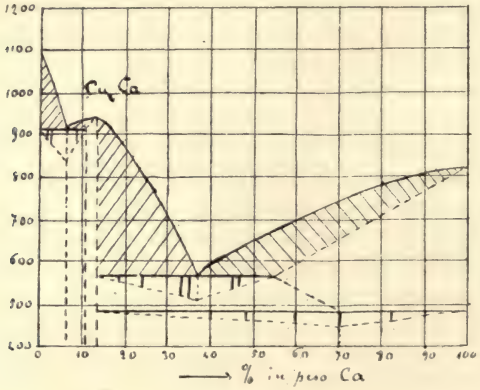

FIG. 71.

56 per cent. On the cooling curve of alloys between 23·5 and 90 per cent. calcium, points of arrest are noted at 480° with a maximum for 70 per cent. of the metal. This alloy, which may be a mixed crystal or the compound $CuCa_4$, has a homogeneous appearance and passes without change of composition from an α to a β form.

Alloys containing about ·8 per cent. calcium are not acted upon by water and are copper-coloured, those with 1·25 per cent. of calcium are a little harder than the pure metal. The others are more brittle, decompose water, and decompose in

[1] *Zeit. anorg. Chem.*, 70, 532 (1911).

air to a powder, which up to 35 per cent. calcium has a brassy colour. From 35 per cent. upwards of calcium the alloys are silvery white when freshly prepared, but decompose when exposed to the air.

Copper-cadmium.—Copper forms two compounds with

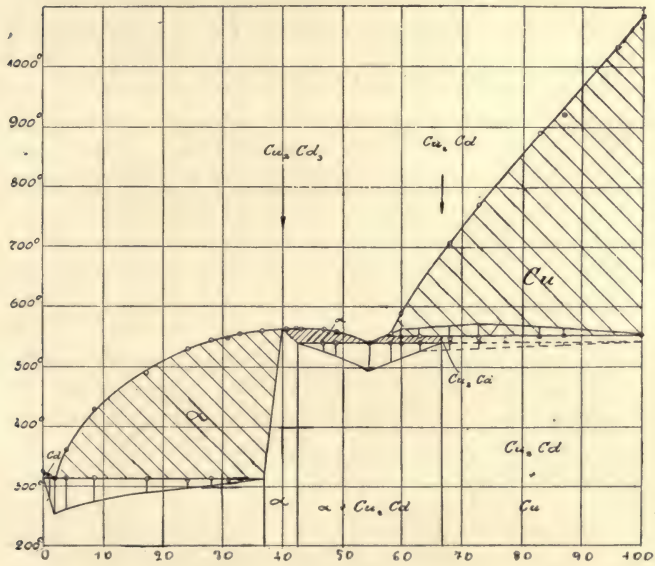

FIG. 72.

cadmium, namely: Cu_2Cd and Cu_2Cd_3. The diagram (Fig. 72) has been drawn from thermal data by Sahmen.[1] From melts containing up to 42 per cent. cadmium, pure copper separates out at temperatures between 1084° and 552°. At 552°, copper, reacting with the melt, forms a compound crystallising in long needles. The eutectic horizontal is prolonged to alloys richer in copper, and ends at 33 per cent.

[1] *Zeit. anorg. Chem.*, **49**, 301 (1906).

cadmium, rendering almost certain the existence of the compound Cu_2Cd. This compound was obtained in crystals by Mylius and Fromm [1] by precipitating a 1 per cent. solution of copper sulphate with cadmium. A slightly defined maximum is observed on the fusion curve, corresponding to the second compound. On both sides of the maximum mixed crystals are formed, on the one side between Cu_2Cd_3 and Cu_2Cd and, on the other, between Cu_2Cd_3 and cadmium. Sahmen believes this formula to be more probably correct than Cu_5Cd_7. The alloys richer in cadmium are soft ; with decreasing content of this metal they become more hard and brittle, but the brittleness decreases on further increase of the copper content. Alloys containing up to 40 per cent. copper are grey, but with increase of copper they become more reddish until the copper colour is reached.

Copper-mercury.—The copper amalgams have not as yet been studied thermally. Chemical and physico-chemical researches on these alloys are, however, numerous.[2] The researches of J. Joule [3] and E. De Souza [4] on the capacity for chemical combination of the two metals should be recorded. The former obtained from liquid amalgams well-defined crystals corresponding to the formula HgCu. The existence of Hg_2Cu_3 is doubtful, a solution of copper in HgCu having probably been mistaken for it. According to De Souza the compounds $HgCu_{14}$ and $HgCu_{16}$ are formed. Copper amalgams on account of their plasticity are frequently used for technical purposes.

Copper-aluminium.—Copper forms with aluminium the three compounds Cu_3Al, CuAl, and $CuAl_2$. The copper-aluminium alloys have been frequently studied by various

[1] *Ber.*, **27, I.**, 630 (1894).

[2] Regnault, *C. R.*, **52**, 533 (1861). Becquerel, *ibid.*, **75**, 1729 (1872). Merz and Weith, *Ber.*, **14**, 1438 (1881). Battelli, *Rend. Acc. Lincei*, (4), **3, II.**, 37 ; **4**, 206 (1887). Bachmetjeff, *Jahrber.*, 109 (1893). Gouy, *Jour. de Phys.*, (3), **4**, 320 (1895). Humphrey, *J. C. S.*, **69**, 343 (1896). Coehn, *Zeit. phys. Chem.*, **38**, 609 (1901). Haber, *ibid.*, **41**, 399 (1902).

[3] *J. C. S.*, **16**, 378 (1863).

[4] *Ber.*, **9**, 1050 (1876).

workers. We may mention the investigations of Le Chatelier,[1] Campbell and Mathews,[2] Guillet,[3] Carpenter and

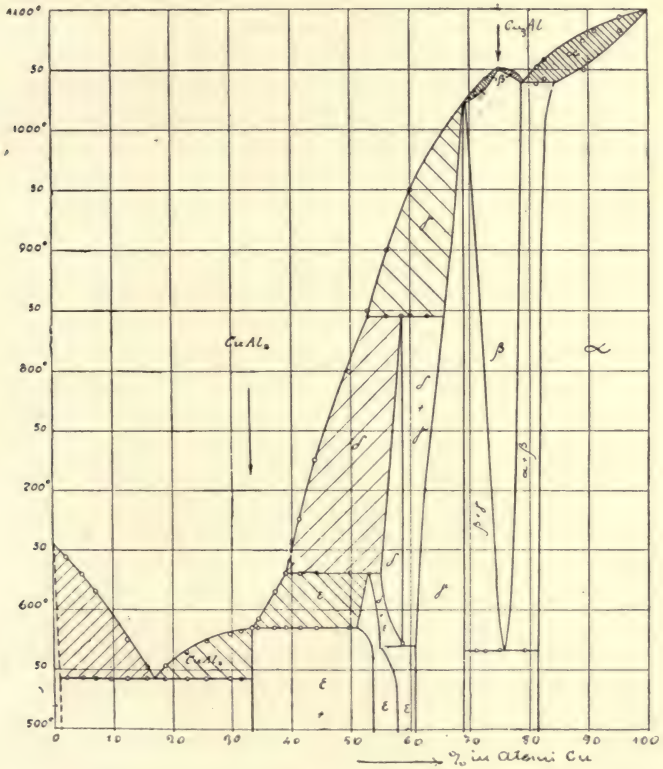

FIG. 73.

Edwards,[4] Curry[5] and, above all, the recent work of Gwyer[6] in Tammann's laboratory at Göttingen.

[1] *Bull. Soc. d'Encour.*, (4), **10**, 573 (1895).
[2] *J. Am. C. S.*, **24**, 253 (1902); **26**, 1290 (1904).
[3] *Rev. de Métallurgie*, 568 (1905). *C. R.*, **14**, 464 (1905).
[4] *Proc. Inst. Mech.*, 57 (1907).
[5] *J. phys. Chem.*, **11**, 425 (1907).
[6] *Zeit. anorg. Chem.*, **57**, 113 (1908).

Gwyer's diagram is shown in Fig. 73, as being that of greatest interest. It shows a maximum, two discontinuities and an eutectic point. The maximum at 1050° and 75 per cent. copper corresponds to the compound Cu_3Al. There exists in all probability a gap in miscibility between 91·5 and 88·5 per cent. of copper; the corre ponding alloys show two species of crystals, one of primary separation surrounded by crystals of the other species. Between 88·5 per cent. and 71 per cent. of copper there is a series of mixed crystals, varying in colour from golden yellow to silvery white. At 625° the saturated mixed crystals react with the melt forming the compound CuAl at a concentration of 50 per cent. At 590° and about 34 per cent. copper the compound $CuAl_2$ separates from the melt and the compound CuAl.

Copper-tin.—The system copper-tin has been investigated by Stanfield,[1] Heycock and Neville,[2] Roberts-Austen,[3] Shepherd and Blough,[4] and Giolitti and Tavanti.[5] The two metals combine to form the compound Cu_3Sn. Fig. 74 gives the diagram constructed by Giolitti and Tavanti from thermal data. It may be divided into two parts, the division being given by the compound Cu_3Sn which corresponds to 25 per cent. of tin. According to the other authors, the crystallisation of a homogeneous body should not take place but an interval of crystallisation should occur. The first part of the diagram, then, extends over the alloys containing up to 25 per cent. of tin. Here solidification begins at points on the line $\gamma\ \beta\ \alpha$, which is made up of three separate branches on which solid solutions occur. The alloy of composition corresponding to the compound behaves as a single, chemically definite substance showing a homogeneous structure when viewed microscopically. The addition to the compound of a small quantity of tin lowers its solidifica-

[1] *Proc. Inst. Mech. Eng.*, 269 (1895).
[2] *Phil. Trans.*, 189 (1897); 202 (1903).
[3] *Proc. Inst. Mech. Eng.*, 67 (1897).
[4] *J. phys. Chem.*, **10**, 630 (1906).
[5] *Gazz. Chim. Ital.*, **38**, II., 209 (1908).

tion point. Alloys containing more tin than the compound give solid solutions between the compound and tin. There is an eutectic between the compound and tin; other authors place it somewhat nearer to pure tin. Between about 53 per cent. and 72 per cent. of copper, Shepherd and Blough

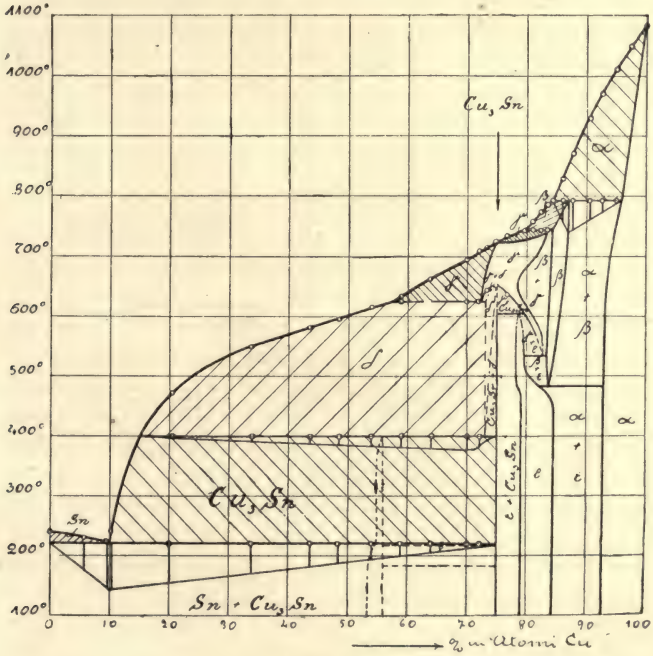

FIG. 74.

observed further transformations without, however, succeeding in elucidating their nature.

The discussion of the particular regions of existence on the diagram of the system with regard to the formation of isomorphous mixtures would occupy too much space and would not be useful for the present work; the problem cannot indeed be regarded as completely solved.

Copper-antimony.—Copper forms with antimony the two compounds Cu_2Sb and Cu_3Sb, of which the latter agrees with the saline valency of monovalent copper. The system has been studied by Baikoff,[1] Hjorns,[2] and Parravano and Viviani.[3] It is not certain at what concentration antimony

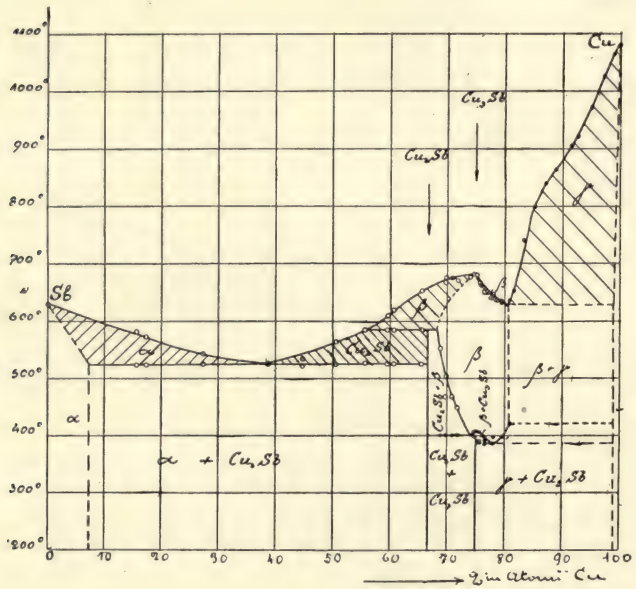

FIG. 75.

dissolves in copper; Parravano and Viviani contend that the amount of such solution is negligible. The compound Cu_3Sb (see Fig. 75) is indicated by a maximum at 682° and 25 per cent. of antimony. It forms solid solutions with antimony and with excess of copper, and undergoes a transformation at 407°. According to Baikoff there is at 390° in

[1] *Bull. Soc. d'Encour.*, I., 626 (1903).
[2] *J. S. C. Ind.*, **25**, 616 (1906).
[3] *Gazz. Chim. Ital.*, **40**, II., 446 (1910).

this region a dystectic point for 23 per cent. of antimony. However, as Guertler[1] observes, the phenomena in this region are not clearly defined. The other compound, for which, however, there are not reliable data, would appear to separate at 587° and 33·3 per cent. of antimony. It is uncertain whether solid solutions exist between antimony and copper. Parravano and Viviani hold that in every case they are formed to a limited extent. Hjorns has argued their existence from the occurrence of brown spots in crystals of antimony. Guertler, however, is of opinion that such spots are due to local oxidation.

Compounds of Silver.

Silver-magnesium. — Silver combines with magnesium, forming two compounds, AgMg and $AgMg_3$. The system has been studied by Zemczuzny,[2] and the diagram is shown in Fig. 76. Boudouard[3] had previously reported the existence of three compounds, $AgMg_2$, AgMg and Ag_2Mg. A distinct maximum is seen on the diagram, corresponding to the compound AgMg ; there is a transformation point for the compound $AgMg_3$ and two eutectic points. At 466°, at a concentration of 17·3 per cent. silver, the alloy which solidifies is an eutectic mixture of magnesium and the compound $AgMg_3$. An arrest is noted without any maximum corresponding to the compound $AgMg_3$, which melts with decomposition at 492° and 22·5 per cent. of silver. At about 820° and 50 per cent., the compound AgMg separates ; on both sides of it solid solutions are formed. This might lead to the supposition that we are here dealing with one of the types of solid solution laid down by Roozeboom. In Roozeboom's types, however, the solid solution series are uninterrupted, while here there are gaps in the series. An analogous case has been brought to light by Baikoff[4] in the fusion of the

[1] *Métallographie*, Vol. I., Part I., p. 756.
[2] *Zeit. anorg. Chem.*, **49**, 400 (1906).
[3] *Bull. Soc. d'Encour.*, 200 (1903).
[4] *Journal of the Russian physico-chemical Society*, **36**, 111 (1904).

copper-antimony alloys. These alloys are very hard, and become increasingly so as they approach in composition to the definite compounds. They vary in colour from white (in the case of almost pure silver) to yellow. Alloys rich in magnesium are very brittle and decompose water more readily than pure magnesium. They are oxidised to a black powder on exposure to air.

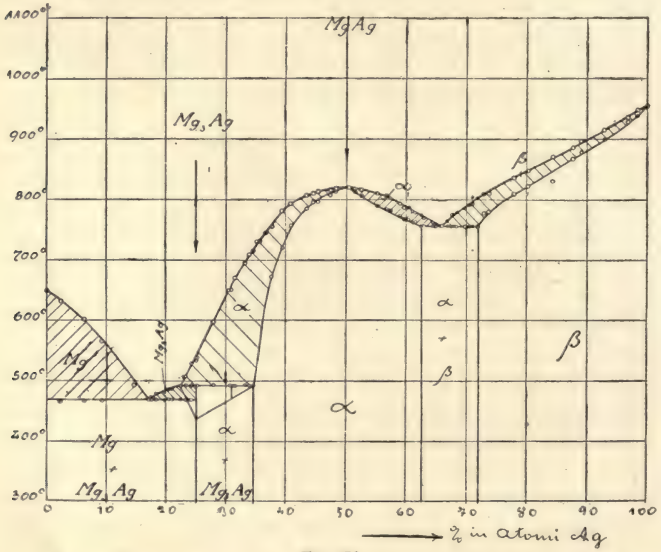

FIG. 76.

Silver-calcium.—This system was studied by Baar,[1] who observed the formation of the following compounds: Ag_4Ca, Ag_3Ca, Ag_2Ca, AgCa and $AgCa_2$. On the fusion diagram (see Fig. 77), there separates at *C* an eutectic conglomerate of crystals of silver and the compound Ag_4Ca. At 20 per cent. of calcium and 650°, the compound Ag_4Ca is formed. At 683°, crystals of Ag_3Ca separate which coexist with the melt. At 25 per cent. and 725°, crystals of Ag_3Ca

[1] *Zeit. anorg. Chem.*, **70**, 352 (1911).

are in equilibrium with a melt of the same composition. A further addition of calcium gives rise to a discontinuity at a point which corresponds to the compound Ag_2Ca, at 596° and 33·5 per cent. calcium. From the eutectic point *H* the curve rises, indicating a new crystalline species; the maximum at 50 per cent. and 665° is due to the compound AgCa. The curve then falls to 70·5 per cent., separating mixed crystals. From 54 per cent. to 64 per cent. of calcium, arrest points occur corresponding to the formation of the compound $AgCa_2$.

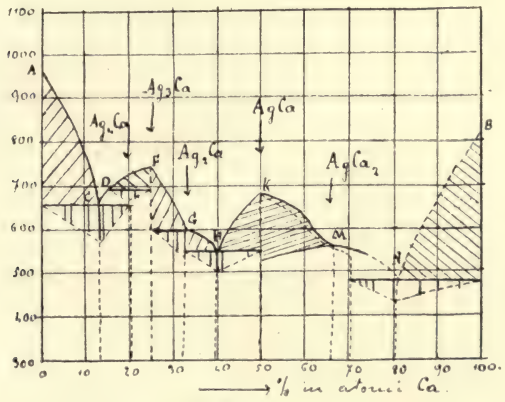

FIG. 77.

The silver-calcium alloys are not so ductile as silver. They are increasingly brittle up to 86 per cent. of calcium, whence their brittleness decreases. Up to 36 per cent. of calcium these alloys are unattacked by water, but with more calcium they react with water and are oxidised in the air to a grey powder.

Silver-zinc.—Silver forms numerous compounds with zinc. They comprise Ag_3Zn_2, AgZn, Ag_2Zn_3 and Ag_2Zn_5, in which the saline valency of the two metals is not exhibited at all. The system silver-zinc studied by Gautier [1] and Heycock

[1] *Bull. Soc. d'Encour*, 1315 (1896).

and Neville [1] has since been well worked out by Petrenko.[2] The diagram is given in Fig. 78. No maximum is shown, but five points of discontinuity, of which three, β, γ and δ, are evident and well defined by thermal horizontals; the other two are less clear. The compounds correspond with the various points of discontinuity. At 28·1 per cent.[3] zinc and 710° there separates Ag_3Zn_2, at 37·7 per cent. and 694° AgZn, at 47·61 per cent. and 665° Ag_2Zn_3, and at 60 per cent.

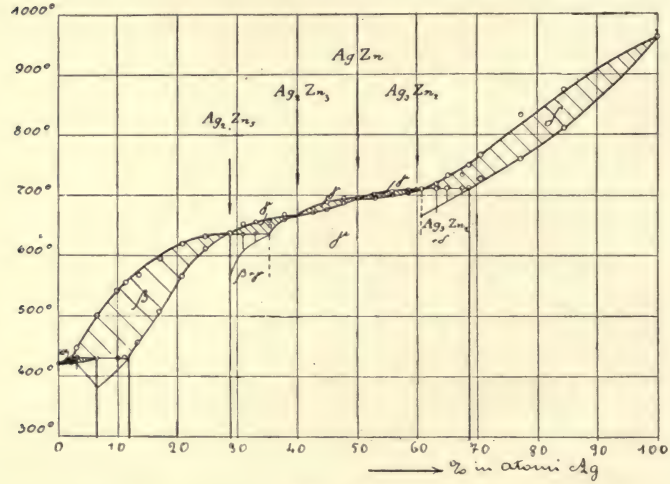

FIG. 78.

and 638° Ag_2Zn_5. The crystalline conglomerates consist alternately of homogeneous mixed crystals and of the two structural elements.

Alloys rich in zinc are harder than alloys containing smaller proportions of this metal; the maximum hardness occurs between 47·6 and 60 per cent. of zinc. The colour of alloys varies from silvery white to bluish grey.

[1] *J. C. S.*, **71**, 407 (1897).
[2] *Zeit. anorg. Chem.*, **48**, 347 (1906).
[3] The percentages here are percentages by weight, not atomic percentages.

Silver-cadmium.—Silver combines with cadmium, forming the compounds $AgCd_4$, $AgCd_3$, Ag_2Cd_3 and AgCd. The system has been investigated by Gautier,[1] Kirke Rose,[2] Bruni and Quercigh,[3] and Petrenko and Feodoroff.[4] The diagram is given in Fig. 79. Silver and cadmium mix in all proportions in the fluid state ; in the solid state they form a series of solid solutions. At 200° and about 50 per cent. the compound AgCd is formed. On the cooling curve between 500° and 600°, are two arrests which, although there are no transformation points, may represent the compounds $AgCd_4$ and $AgCd_3$, the latter being admitted by Maey from his determinations of specific volume. At the point *F*, at about 35 per cent. silver and 630°, there separates the compound Ag_2Cd_3, of a rose colour and very brittle. The mixed crystals *g'* and *g*, which are formed at 57 per cent. and 64 per cent. respectively of silver, are very near to the compounds Ag_3Cd_2 (59·02 per cent. Ag) and Ag_2Cd (65·7 per cent. Ag) reported by Kirke Rose. The composition of the saturated mixed crystals *g'* changes with fall of temperature, while the crystals *g* retain constant composition.

Silver-mercury.—Amalgams of silver, such as ˙arguerite, crystallising in the regular system, are found in nature. The formation of chemical compounds between the two metals is certain, although the system has not as yet been studied by methods of thermal analysis.

Silver dissolves easily in mercury at boiling temperature, and from the solution may be obtained beautiful needle-shaped crystals known as "Diana's tree." Numerous researches have been made to establish the existence of chemical compounds in silver amalgams.[5] The existence of

[1] *Bull. Soc. d'Encour.*, (5), I., 1315 (1896).
[2] *Proc. Roy. Soc.*, **74**, 218 (1905).
[3] *Zeit. anorg. Chem.*, **68**, 198 (1910).
[4] *Ibid.*, **70**, 257 ; **71**, 215 (1911).
[5] Bottger, *J. Pr. Chem.*, **3**, 278 (1834) ; Croockewit, *Ann. Chem.*, **68**, 289 (1848) ; Joule, *Rep. Brit. Ass.*, II., 55 (1850) ; Rammelsberg, *Pogg. Ann.*, **120**, 54 (1863) ; Becquerel, *C. R.*, **75**, 1729 (1872) ; De Sousa, *Ber.*, **8**, 1616 (1875) ; Merz and Weith, *Ber.*, **14**, 1438 (1881) ; Schumann, *Wied. Ann.*, **43**, 101 (1891) ; Gouy *J. de Phys.*, (3), **4**, 320 (1895) ; Littleton, *J. C. S.*, **67**, 239 (1895) ; Berthelot, *C. R*, **132**, 241, 290 (1901) ; *Ann. Chim. Phys.*, (7), **22**, 317 (1901) ; Coehn, *Zeit. phys. Chem.*, **38**, 609 (1901).

the compounds $HgAg_2$, HgAg and Hg_3Ag_2 is probable. An amalgam of the composition Hg_3Ag_2 in well-defined crystals

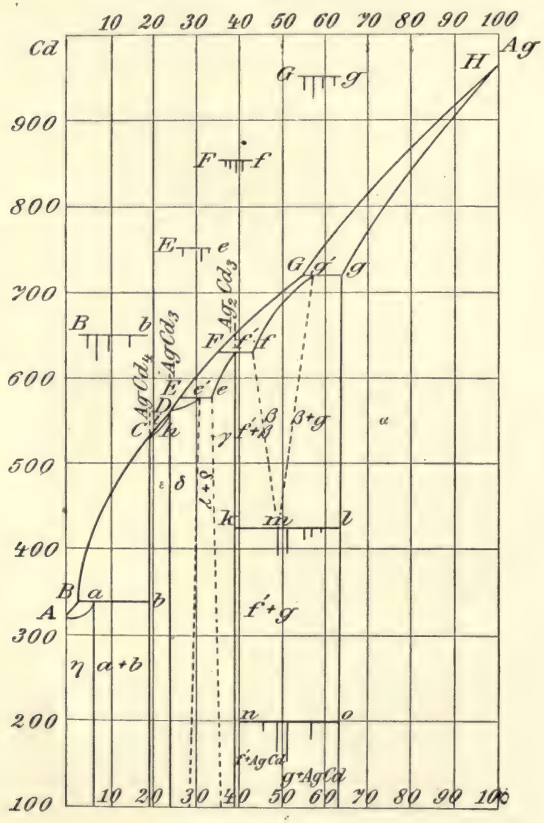

FIG. 79.

was isolated by Dumas.[1] Ogg [2] prepared various amalgams of silver by electrolytic methods.

[1] *C. R.*, **69**, 759 (1869).
[2] *Zeit. phys. Chem.*, **27**, 301 (1898).

Silver-aluminium.—Aluminium and silver form the compounds Ag_2Al and Ag_3Al, the latter of which exhibits the saline valency of the two elements. Fig. 80 is the diagram constructed by Petrenko [1] from thermal data. The pre-

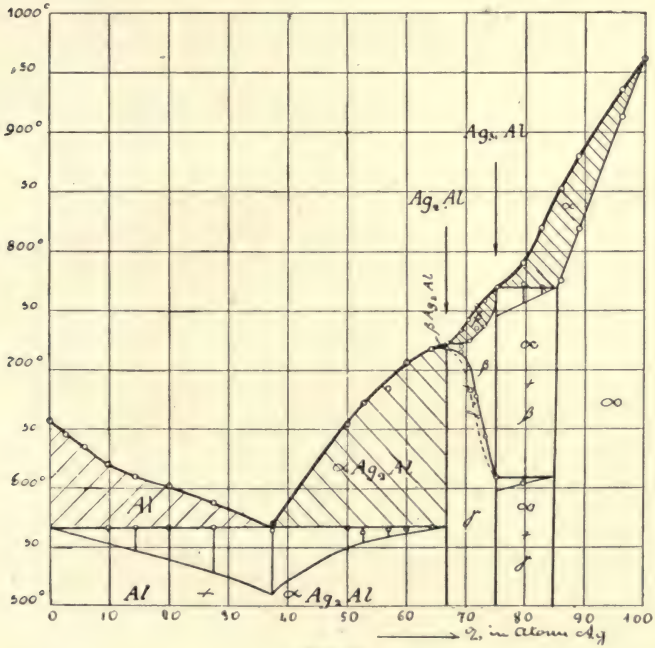

FIG. 80.

ceding investigations of Gautier,[2] Guillet,[3] and Heycock and Neville [4] may also be mentioned. The diagram shows that the two compounds mentioned above are formed. The cooling curves of the compounds are similar in character to those for other simple substances, showing only single arrest

[1] *Zeit. anorg. Chem.*, **46**, 49 (1905).
[2] *Bull. Soc. d'Encour.*, 1312 (1896).
[3] *Génie Civil*, 1902.
[4] *Phil. Trans.*, A, **69** (1897).

points. The interval of eutectic crystallisation at 567° is for the first compound reduced to zero at the point β, while for the second compound at 75 per cent. silver and 770°, the interval is greater than for all other melts. Transformation points are shown at 718° and 610° respectively. These alloys consist in section of a single species of crystals.

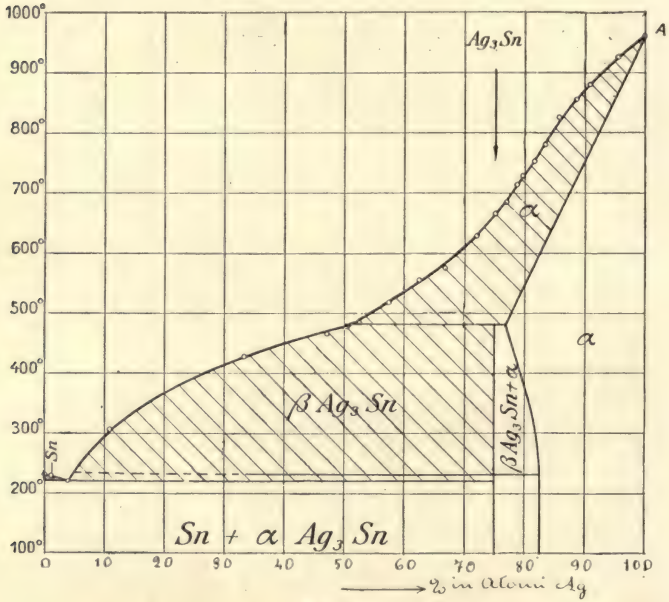

FIG. 81.

The two alloys form mixed crystals between 610° and 718°. It is uncertain whether the transformation of mixed crystals takes place with or without separation of their components, $AlAg_2$ and $AlAg_3$. On the curve above 718° β crystals of $AlAg_2$ are in equilibrium with the melt, while below 718°, γ crystals are similarly in equilibrium. The presence of this branch indicating the equilibria of the γ crystals cannot,

however, be demonstrated directly. A horizontal indicates the transformation of β into α crystals.

Microscopic examination confirms the foregoing deductions, since it reveals the presence of the five groups of alloys which are presumed to exist from thermal considerations.

Silver-tin.—Silver forms the compound Ag_3Sn with tin as may be gathered from Fig. 81, which reproduces the diagram constructed by Petrenko[1] from thermal data. Heycock and Neville [2] had previously studied the system. There are two branches on Petrenko's diagram, the one straight and the other sinuous; at 480°, 232° and 220° respectively, horizontals occur. At 480° and 27 per cent. of tin, the compound Ag_3Sn separates. Microscopic examination shows that the alloy of this composition consists of polyhedra. The compound is dimorphic. A maximum interval of transformation occurs at 232° at a concentration corresponding to the compound.

Silver-antimony.—Silver combines with antimony to form the compound Ag_3Sb, as appears from the investigations of Gautier,[3] Heycock and Neville,[4] and, finally, of Petrenko.[5] Maey [6] from volumetric observations argues that silver and antimony form a single compound Ag_3Sb. Pushin,[7] however, from his measurements of electro-motive force, argues that there are two compounds, Ag_2Sb and Ag_3Sb.

Petrenko's diagram, shown in Fig. 82, demonstrates that by addition of antimony the melting point of silver is lowered sharply. Mixed crystals containing antimony separate, which are recognisable by microscopic examination. At 560° and 27·07 per cent. of antimony, there is a sharp arrest point corresponding to the compound Ag_3Sb. From 27·07 to 45 per cent. antimony the compound separates and at 485°, the eutectic alloy. Microscopic

[1] *Zeit. anorg. Chem.*, **53**, 200 (1907).
[2] *Phil. Trans.*, **189**, A, 140 (1897).
[3] *Bull. Soc. d'Encour.*, 1896, pp. 1309, 1310.
[4] *Phil. Trans.*, **189**, A, 25 (1897).
[5] *Zeit. anorg. Chem.*, **50**, 139 (1906).
[6] *Zeit. phys. Chem.*, **50** (1905).
[7] *Journ. Russ. phys. Chem. Soc.*, May, 1905.

examination confirms these data. The compound appears in polygonal crystals separated by fine lines.

Silver-manganese.—It is not certain whether silver forms compounds with manganese. The system was studied by thermal and miscroscopic methods by Hindrichs [1] and Arrivaut [2]; the latter also used chemical methods and determined electrolytic potentials. Hindrichs does not

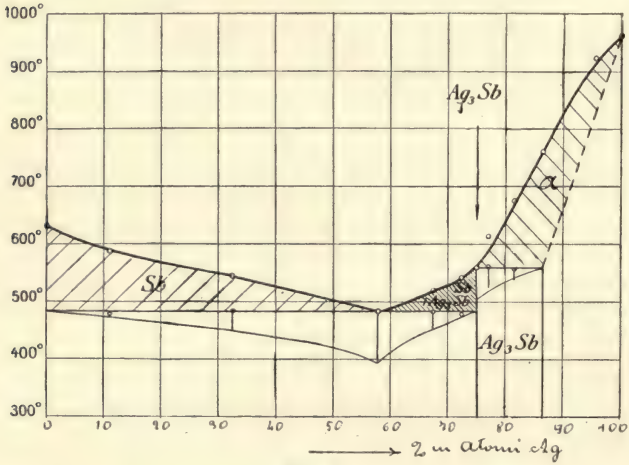

FIG. 82.

report the formation of compounds, but states that two strata exist with limited mutual solubility. Arrivaut, while admitting the limited miscibility of the two metals, maintains that at 978° and at 20 per cent. of manganese, the compound Ag_2Mn is formed. The compound forms a continuous series of mixed crystals with silver. Guertler,[3] however, is of opinion that the supposed compound is, rather, a saturated solution of manganese in silver.

[1] *Zeit. anorg. Chem.*, **59**, 437 (1908).
[2] *Ibid.*, **83**, 193 (1913).
[3] *Metallographie*, Berlin, 1912, Vol. I., Part I., p. 98.

By analogy with gold, the existence of a combination between silver and manganese is probable.

Silver-platinum.—There is some doubt as to the occurrence of chemical combination between silver and platinum. According to Doerinckel's[1] investigations, the compound Ag_2Pt is formed between the two metals. Thompson and

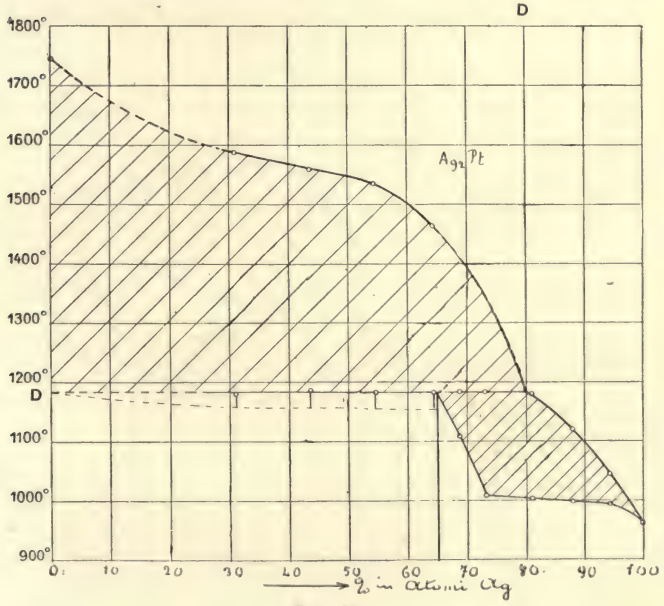

FIG. 83.

Miller[2] stated that such a compound was formed and noted that platinum, when alloyed with silver, was soluble in nitric acid. Fig. 83 is Doerinckel's diagram. It cannot be drawn above 80 per cent. platinum on account of the high melting point of such alloys. At 1184° and 20 per cent. platinum there is a distinct discontinuity. Up to 35 per cent. there is a continuous series of mixed crystals, the last member of

[1] *Zeit. anorg. Chem.*, **54**, 338 (1907).
[2] *J. Amer. C. S.*, **28**, 1115 (1906).

which contains 48 per cent. by weight of platinum. This corresponds fairly nearly to the formula Ag_2Pt, which would require 47·5 per cent. of platinum. It is doubtful, however, whether this is a compound or mixed crystal.

The alloys from 10 to 30 per cent. are a little harder than their components. From 40 per cent. of platinum the hardness increases slowly and at 70 per cent. exceeds that of calc spar.

Compounds of Gold.

Gold-magnesium.—Magnesium forms four compounds with

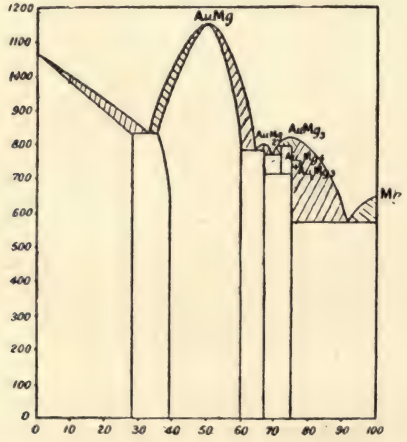

Fig. 84.

gold, in none of which saline valencies are shown. They are AuMg, $AuMg_2$, $AuMg_3$ and Au_2Mg_5. The system has been studied by Vogel,[1] by Urasoff[2] and by these two authors in collaboration.[3] The results obtained are in general agreement (see Fig. 84). Vogel admits the first three compounds,

[1] *Zeit. anorg. Chem.*, **63**, 169 (1909).
[2] *Ibid.*, **64**, 375 (1909).
[3] *Ibid.*, **67**, 442 (1910).

while Urasoff adds Au_2Mg_5 which would appear to separate at 796° and 72 per cent. of magnesium. For the first three compounds, whose concentrations are respectively 50, 67 and 75 per cent. of magnesium, Vogel gives the melting points as 1160°, 796° and 830°, while Urasoff gives 1150°, 788° and 818°. Between 30 and 34 per cent. of magnesium Vogel has observed that although the alloys at 830° are homogeneous, when cooled slowly to 818°, they separate out crystals, which would show a diminution in the solubility of the alloys from 0 to 30 per cent. in the foregoing alloys. At 720° and 72 per cent. of magnesium, Urasoff observed a thermal effect due to a transformation of the compound Au_2Mg_5.

Gold forms solid solutions with magnesium from 17 to 27 per cent. magnesium; magnesium in the crystalline state does not dissolve notable quantities of gold.

Gold-zinc.—Gold and zinc form the following compounds: AuZn, Au_3Zn_5 and $AuZn_8$. The system was studied by Vogel [1] and the diagram is shown in Fig. 85. At 50 per cent. zinc and 744° there is a maximum corresponding to the compound AuZn which, by reaction with the melt, gives mixed crystals with gold and zinc. Between 50 and 63 per cent. of zinc, mixed crystals separate with a higher content of zinc than is demanded by the formula AuZn, and at about 650°, a homogeneous substance crystallises which is the compound of the formula Au_3Zn_5. At 486° saturated mixed crystals γ are changed into a third compound. The maximal transformation is at 88 per cent. of zinc corresponding to the formula $AuZn_8$. Here a new series of mixed crystals occurs. Alloys rich in gold have the same hardness as that metal, are less tenacious, and not at all brittle. At above 31 per cent. of zinc the alloys show considerable hardness and brittleness. After 61 per cent. they become gradually less hard and brittle.

Gold-cadmium.—Gold forms two compounds with cad-

[1] *Zeit. anorg. Chem.*, **48**, 319 (1906).

mium, Au_4Cd_3 and $AuCd_3$ as shown by Vogel,[1] who has constructed the diagram shown in Fig. 86 from thermal data. The crystallisation of the two compounds is marked by two distinct discontinuities, one at 43 per cent. cadmium and 623°, and the other at 75 per cent. cadmium and 493°. From 0 to 28 per cent. cadmium, a series of mixed crystals is formed. Au_4Cd_3 forms with the saturated mixed crystal β, occurring at 51 per cent. cadmium, a series of mixed crystals

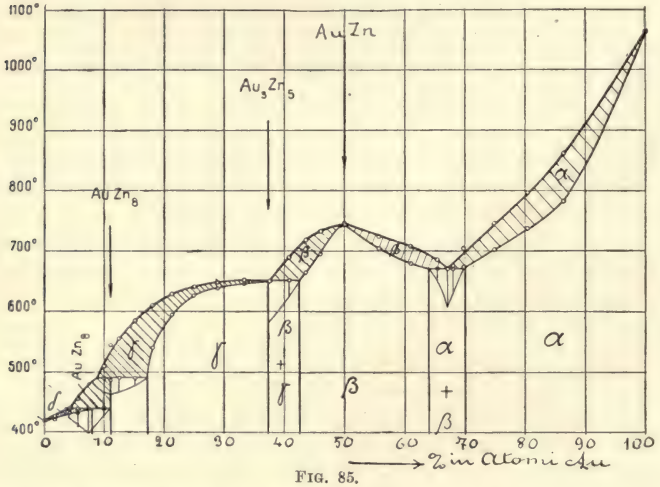

FIG. 85.

rich in cadmium, while $AuCd_3$ crystallises in eutectic alloy from melts rich in cadmium. The compound AuCd, whose formation was reported by Heycock and Neville,[2] might be, according to Vogel, a mixed crystal containing Au_4Cd_3 of the β series, richer in cadmium, and only having the composition corresponding to AuCd fortuitously. The more recent studies on the gold-cadmium alloys made by Saldau [3] have regard to thermal phenomena, hardness, the special properties of

[1] *Zeit. anorg. Chem.*, **48**, 333 (1906).
[2] *J. C. S.*, **61**, 888 (1892).
[3] *Int. Zeit. f. Metallogr.*, VII., 3 (1914).

eutectic alloys, electrolytic potential and microscopic structure. Saldau, from his investigations, maintains that these alloys include the compounds AuCd and $AuCd_3$. He derives the former not only from the fusion diagram, but also from the diagrams for hardness and electrical conductivity. The first compound separates at 50 per cent. and about 625° and

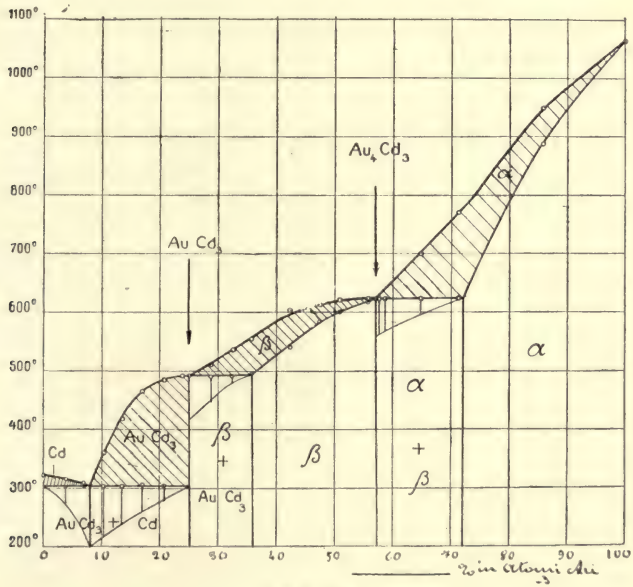

FIG. 86.

the second at 75 per cent. of cadmium and 490°. According to Saldau the compound stated by Vogel to be Au_4Cd_3 has no real existence, for this concentration simply represents the limit of saturation of the compound AuCd with gold in mixed crystals. The two compounds form mixed crystals with the components, AuCd between 46 and 59 per cent. cadmium, and $AuCd_3$ between 74 and 79 per cent. cadmium. Two other series of mixed crystals exist, one between gold

and cadmium up to 35 per cent. of cadmium, and the other between cadmium and gold up to 2 per cent. gold.

The alloys show maximum hardness at 18 to 30 per cent. of cadmium and 51 to 63 per cent. cadmium ; the maximum brittleness occurs at 51 to 63 per cent. cadmium.

Gold-mercury.—Gold amalgams occur naturally as solids

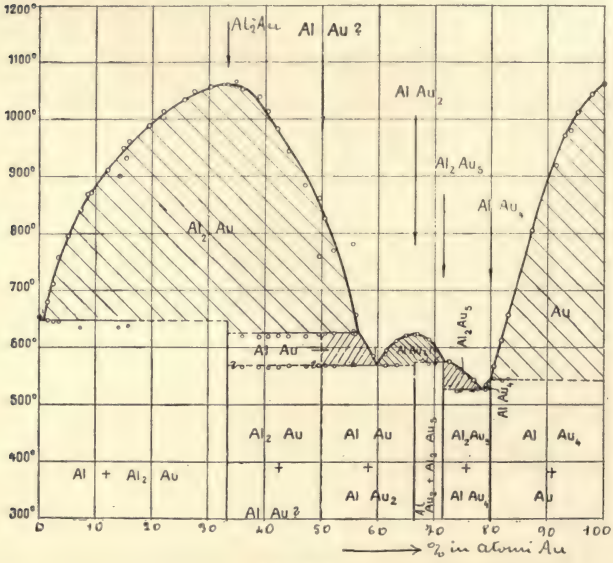

FIG. 87.

or semi-solids according to their mercury content ; the solid amalgams are well crystallised.

The two metals combine chemically, but the system has not yet been studied thermally. Böttger[1] prepared artificial amalgams by direct union of the two elements. Croockewit[2] isolated a compound of the formula $AuHg_2$.

[1] *Jour. pr. Chem.*, **3**, 278 (1834).
[2] *Ibid.*, **45**, 87 (1847).

The numerous investigations [1] on these amalgams lead us to suppose the existence of other combinations richer in gold. The existence of the compounds Au_2Hg and Au_4Hg seems probable. The gold amalgams have always been of great importance in the extraction of gold from its minerals.

Gold-aluminium.—The system gold-aluminium was studied by Heycock and Neville [2] thermally and micrographically. The two metals form the compounds Au_4Al, Au_5Al_2, Au_2Al, $AuAl$, $AuAl_2$. The curve shows two distinct maxima, one at about 1060° and 33·3 per cent. gold and the other at about 625° and 66 per cent. of gold, corresponding to the compounds $AuAl_2$ and Au_2Al respectively. There are three discontinuities at which the other compounds separate. The first occurs at about 56 per cent. of gold and 625° ; probably it corresponds to the compound AuAl. Heycock and Neville noticed, however, that there is not a perfect equilibrium between $AuAl_2$ and the eutectic at 569°, for on microscopical examination they detected the presence of $AuAl_2$ characterised by its purple colour. The compound AuAl, indeed, does not separate in a pure state. The eutectic horizontal at 569°, which should only extend to 50 per cent. of gold, reaches 40 per cent., which is explained by the fact that at that point the equilibrium is complete. The other two compounds Au_5Al_2 and Au_4Al separate respectively at 575° and 72 per cent. of gold and 545° and 78·5 per cent. gold.

Gold-tin.—The following compounds are formed between gold and tin : $AuSn$, $AuSn_2$ and $AuSn_4$. They have been recognised by Vogel [3] by means of thermal analysis. Fig. 88 represents the equilibrium diagram. Preceding Vogel's work, the system had been studied from the point of view of

[1] Henry, *Phil. Mag.*, (4), **9**, 458 (1855) ; Knafel, *Dingl. Poly. Journ.*, **168**, 282 (1863); Rammelsberg, *Pogg. Ann.*, **120**, 54 (1863) ; De Souza, *Ber.*, **9**, 1050 (1876) ; Chester *Ann. Jour. Sci.*, (3), **16**, 29 (1878) ; Kasauzeff, *Bull. Soc. Chim.*, (2), **30**, 20 (1878) ; Merz and Weith, *Ber.*, **14**, 1438 (1881) ; Wilm., *Zeit. anorg. Chem.*, **4**, 325 (1893) ; Gouy, *Jour. de Phys.*, (3), **4**, 320 (1895).

[2] *Phil. Trans.*, A, **194**, 201 (1900).

[3] *Zeit. anorg. Chem.*, **48**, 60 (1905).

electrical conductivity by Matthiessen,[1] while Maey [2] and Heycock and Neville [3] studied the specific volume, and Lawrie [4] the electrolytic potential. The fusion curve falls from the melting point of pure gold to an eutectic point, and

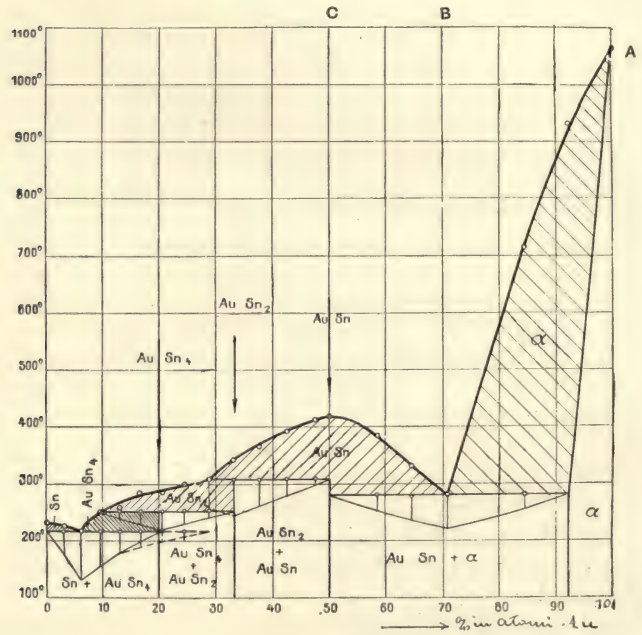

FIG. 88.

subsequently rises to a distinct maximum. In the rest of the curve two discontinuities occur which are met by thermal horizontals from 10 to 33 per cent. and from 30 to 50 per cent. respectively. From melts rich in gold, mixed crystals separate containing up to 8 per cent. of tin. The

[1] *Pogg. Ann.*, **110**, 190 (1860); *Phil. Trans.*, **150**, 161 (1860).
[2] *Zeit. phys. Chem.*, **38**, 292 (1901).
[3] *J. C. S.*, **59**, 936 (1891).
[4] *Phil. Mag.*, (5), **33**, 94 (1892).

compound corresponding to the maximum has the formula AuSn and contains 37·63 per cent. by weight of tin ; it melts at 418°. At the temperature of the eutectic horizontal, crystals of AuSn react with the melt and pass into a compound richer in tin of the formula $AuSn_2$, containing 54·68

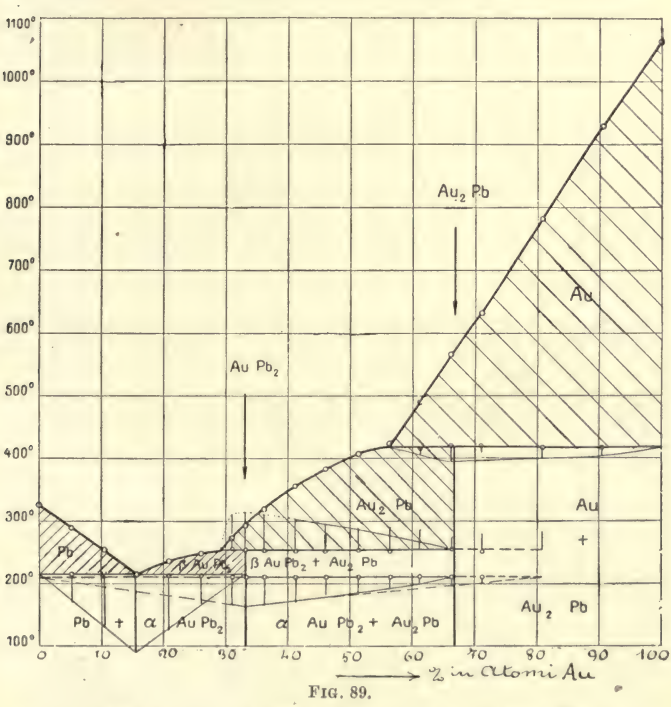

FIG. 89.

per cent. by weight of tin and melting at 308°. This compound passes in turn into a third compound, $AuSn_4$, which melts at 252°. All these alloys are very brittle and acid resistant, particularly the alloy AuSn, which is as brittle as glass.

Gold-lead.—Lead and gold form the compounds Au_2Pb

and $AuPb_2$. Vogel [1] has made a thermal study of this system. Maey [2] concluded from a study of specific volumes that the compound Au_2Pb_3 should also occur.

The diagram is reproduced in Fig. 89. Two very distinct discontinuities are seen ; the first is at 418° and corresponds

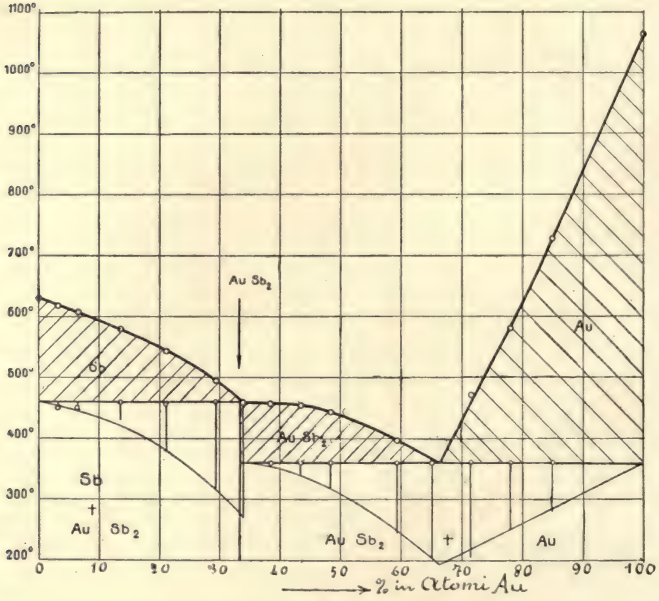

FIG. 90.

to the compound Au_2Pb with a maximal arrest for 35 per cent. lead. At 211° and the same concentration, a polymorphic transformation takes place. The second discontinuity is at 254° and the corresponding thermal arrest, with a maximum at 67·8 per cent. of lead, indicates the compound $AuPb_2$. This compound also undergoes a polymorphic transformation at 211°. The compound Au_2Pb crystallises

[1] *Zeit. anorg. Chem.*, **45**, 11 (1905).
[2] *Zeit. phys. Chem.*, **38**, 292 (1901).

in large white crystals, $AuPb_2$ in long needles. The two compounds form mixed crystals with each other and with the components.

Maey's supposed compound Au_2Pb_3 is explained by Vogel, who argues that the specific volume method can be used for alloys with two structural elements, but not for alloys such as those of this system between 10 to 72 per cent. lead having three such structural elements. Both compounds are brittle—Au_2Pb more so than $AuPb_2$.

Gold-antimony.—These metals according to Vogel[1] form the compound $AuSb_2$. It is seen from the diagram (Fig. 90) that each metal lowers the melting point of the other. Primary separation of gold and antimony occurs at 0—34 per cent. antimony and 73—100 per cent. antimony respectively. Melts containing 35 per cent. of gold separate the compound $AuSb_2$ at 460°. The primary separation of this compound continues till 34 per cent. of antimony is reached, when eutectic solidification occurs at a temperature of 360°. The compound $AuSb_2$ is harder than its constituents ; it is very brittle and more resistant than antimony to the action of acids. In section it has a shining shell-like crystalline appearance.

Gold-manganese.—Manganese combines with gold to form the compound AuMn. This system was studied by Parravano and Perret.[2] The capacity of gold for combination with manganese differentiates it from the first member of its group, namely, copper, which does not combine with manganese, but forms a continuous series of mixed crystals. In the case of silver, as mentioned above, its capacity for combination with manganese is not yet well established. In the fusion diagram (Fig. 91) described by Parravano and Perret, there is in addition to the formation of the compound AuMn, a lack of miscibility between 50 and 57·5 per cent. by weight of manganese. Further, transformations have

[1] *Zeit. anorg. Chem.*, **50**, 151 (1906).
[2] *Gazz. Chim. Ital.*, **45**, I., 293 (1915).

been observed in the solid state which, however, are not yet well explained. Manganese lowers the melting point of gold to 990° for a concentration of 10·5 per cent. manganese. In this interval mixed crystals separate. There is a maximum at 1225° corresponding to the compound (21·8 per cent. by weight manganese); thence the curve falls to 1080° and 46 per cent. by weight of manganese. From this point the curve rises to the melting point of manganese, but between 50 and 57 per cent. of manganese a gap in

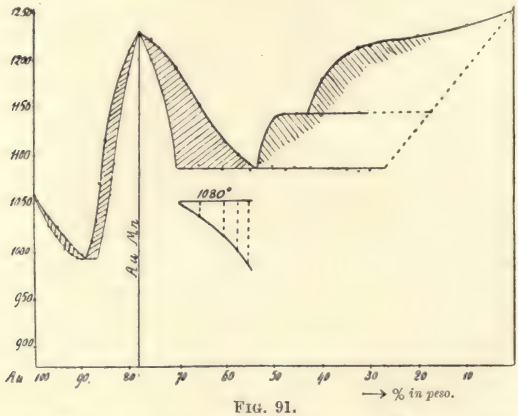

FIG. 91.

liquid miscibility occurs. The formation of the compound has been confirmed by measurements of the hardness of alloys; the hardness curve of alloys up to 35 per cent. manganese is similar to the type represented in Fig. 34.

Compounds of Metals of Group II. with Metals of other Groups.

COMPOUNDS OF BERYLLIUM.

Beryllium-iron.—According to G. Oersheld,[1] the two metals combine chemically, and in all probability the compound

[1] *Zeit. anorg. Chem.*, **97**, 6 (1916).

$FeBe_2$ is produced. The system has been studied up to 21 per cent. of beryllium. At 1155° and a concentration of 38·4 per cent. (atomic) of beryllium, there is an eutectic point; up to 29 per cent., solid solutions are formed. By addition of beryllium the transformation temperature of iron β into iron α is lowered till it becomes constant. The compound is blackened by alkalies.

Compounds of Magnesium.

Magnesium-aluminium. — Aluminium and magnesium form the compound Mg_4Al_3. The system has been studied by Boudouard[1] and Grube.[2] The diagram (Fig. 92), taken

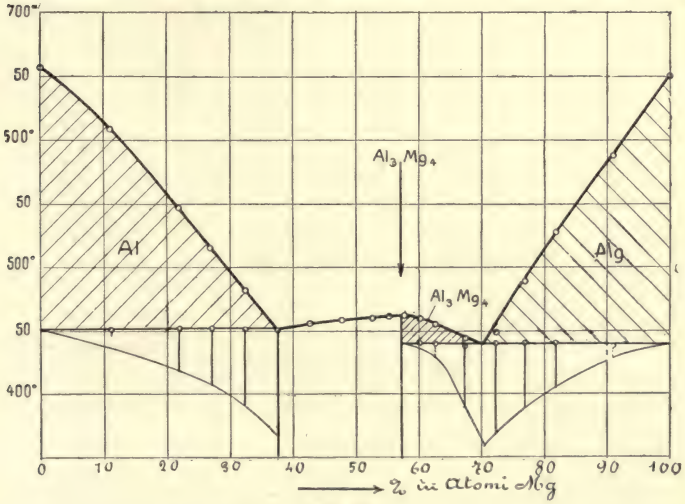

Fig. 92.

from Grube, is of interest because, although the compound has a range of existence of about 30 per cent., it displays no decided maximum; this system approaches, therefore, to the type *c* described on p. 11. The maximum occurs at

[1] *Bull. Soc. Chim.*, (3), **27**, 5, 45 (1902).
[2] *Zeit. anorg. Chem.*, **45**, 225 (1905).

462·7° and 54·9 per cent. of magnesium. All the alloys from 35 to 55 per cent. of magnesium crystallise as chemically homogeneous substances; they are in fact mixtures of Mg_4Al_3 and excess of aluminium.

The compound Mg_4Al_3 has a silvery white colour and is

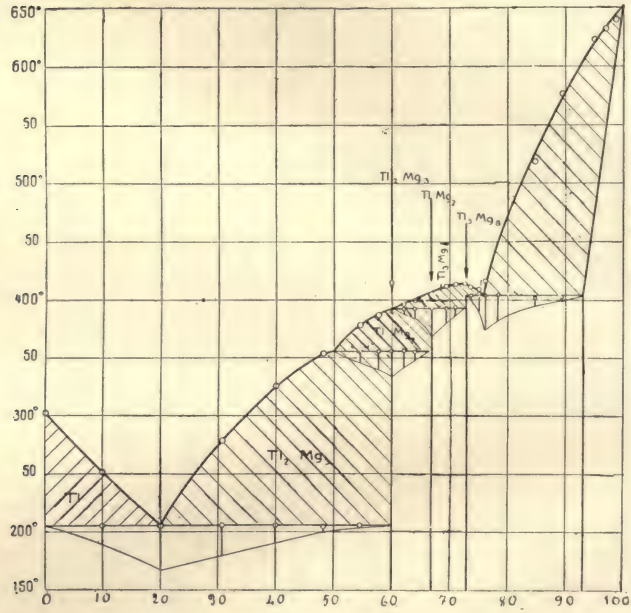

FIG. 93.

very brittle. The brittleness decreases from the composition of the compound to the two pure components. Alloys between 35 and 50 per cent. magnesium have, after polishing, a very bright mirror-like surface.

The alloys of magnesium and aluminium are well known as "*magnalium.*"

Magnesium-thallium. — Magnesium forms the following

compounds with thallium : Mg_3Tl_2, Mg_2Tl and Mg_8Tl_3. The study of the system is due to Grube.[1] The diagram (Fig. 93) shows a distinct maximum corresponding to 27·4 per cent. thallium and two obscured maxima. For the latter, the

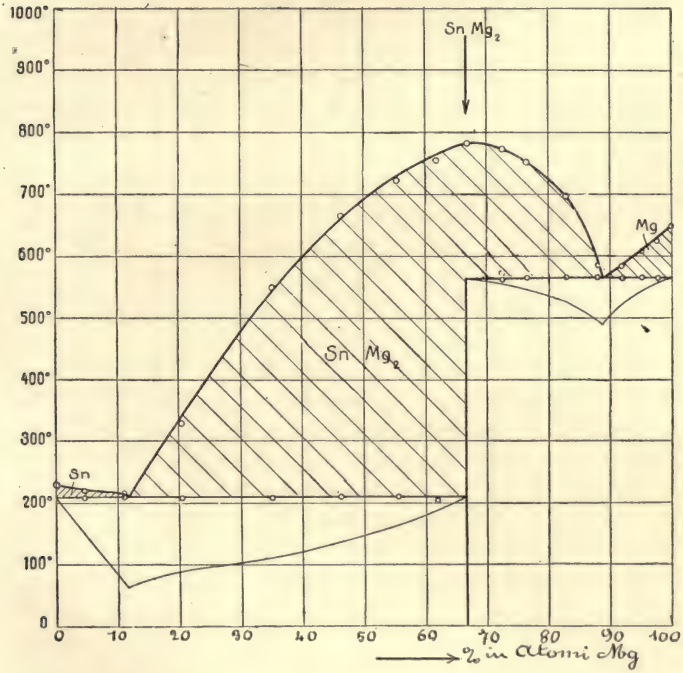

FIG 94.

concentrations are 33·33 per cent. and 40 per cent. thallium respectively, corresponding to the compounds Mg_2Tl and Mg_3Tl_2. The maximum, of course, represents the compound Mg_8Tl_3, which melts to a homogeneous liquid, while the other two break up on fusion into crystals of different composition and into melts. In the region on the

[1] *Zeit. anorg. Chem.*, **46**, 84 (1905).

diagram between the fusion curve and the eutectic horizontals there is equilibrium between one species of crystal and the melt.

These alloys oxidise in air, particularly in a moist atmosphere; the compound Mg_2Tl though not very stable is slightly more resistant than the others.

Magnesium-tin.—Magnesium and tin only form one compound, Mg_2Sn. The system has been investigated by Grube[1] and Kurnakoff and Stepanoff.[2] The diagram (Fig. 94) shows a maximum at 783·4° and a concentration of 66·5 per cent. of magnesium; this corresponds to the compound Mg_2Sn. Below the fusion curve and above the eutectic horizontals there is in every region of the curve one species of crystals in equilibrium with the melt. The alloy Mg_2Sn is formed with great development of heat; it is brittle and has a steel blue colour which is tarnished on exposure by a stratum of black oxide.

The diagram shows three groups of alloys: (1) alloys containing magnesium of primary separation; (2) alloys containing Mg_2Sn of primary separation; and (3) alloys rich in tin containing tin of primary separation.

Magnesium-cerium.—Vogel,[3] who studied this system, has recorded the formation of four compounds, CeMg, $CeMg_3$, $CeMg_9$ and Ce_4Mg. His diagram is shown in Fig. 95. The two branches descending from *A* and *C*, along which cerium and the compound CeMg respectively separate, should apparently intersect in the point *B*. On the cooling curves of these alloys are noted two arrest points, one at about 632° and the other at 497° at a concentration of 20 per cent. magnesium. Vogel explains the presence of a compound here by assuming a decomposition to take place in the solid state. A small branch with a slight maximum at 20 per cent. should fill the gap between *A* and *C*. The compound CeMg separates at a concentration of 50 per cent. and 738°.

[1] *Zeit. anorg. Chem.*, **46**, 76 (1905).
[2] *Ibid.*, **46**, 177 (1905).
[3] *Ibid.*, **91**, 277 (1915).

The arrest point at *E*, which practically occurs a little lower, corresponds with the separation of saturated mixed crystals containing magnesium. From melts with 60 to 75 per cent. —the latter being a maximum on the curve—the compound $CeMg_3$ separates at about 780°. Finally, at 90 per cent. of magnesium, the compound $CeMg_9$ separates.

The compound Ce_4Mg absorbs heat in its formation, *i.e.*, it is endothermic ; it has a very small field of existence and

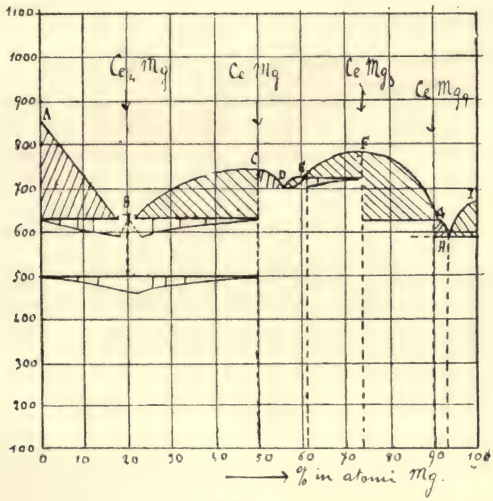

FIG. 95.

a low melting point. This compound, like all the alloys from 20 to about 62 per cent. of magnesium, ignites spontaneously. The compound CeMg is very hard ; a freshly broken surface shows a reddish grey colour. $CeMg_3$ is less hard than CeMg and is not so easily oxidised. $CeMg_9$ is brittle and has a silvery lustre when freshly broken. It is more resistant than the other compounds to oxidation and the action of acids.

Magnesium-lead.—Lead forms with magnesium the com-

pound Mg_2Pb, as was found by Grube [1] and Kurnakoff and Stepanoff.[2] The latter authors consider compounds of the type Mg_2R (where R = Sn or Pb) as belonging to the hypothetical type RH_4 by replacement of four atoms of hydrogen by two atoms of bivalent magnesium. The curve (see Fig. 96) is similar to the curve for magnesium-tin. The

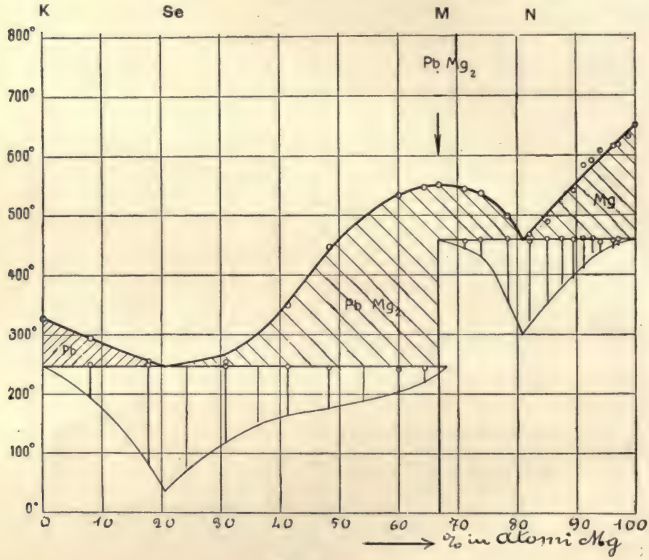

FIG. 96.

diagram consists of three parts ; in the first, lead separates ; in the third, magnesium ; while in the second, with a maximum at 550° and 66·66 per cent. magnesium, the compound Mg_2Pb separates. This compound is oxidised in moist air and has a steel grey colour.

Magnesium-antimony. — Antimony combines with magnesium forming the compound Mg_3Sb_2. The system has

[1] *Zeit. anorg. Chem.*, **44**, 117 (1905).
[2] *Ibid.*, **46**, 177 (1905).

been studied by Grube,[1] and the diagram constructed by him is shown in Fig. 97. A maximum occurs at 961° and 40 per cent. of antimony, corresponding to the compound Mg_3Sb_2. The eutectic horizontals are prolonged to the point indicating the concentration of the compound : there is, consequently,

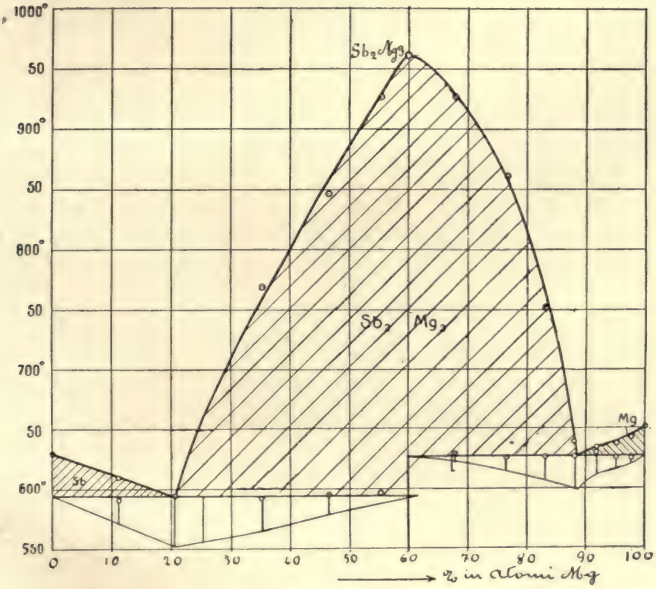

FIG. 97.

no formation of mixed crystals. The compound crystallises in steel grey needles which are oxidised in the air. Alloys increase in brittleness up to 49·5 per cent. of antimony, and between this percentage and 95 per cent. of antimony are exceedingly brittle.

Magnesium-bismuth.—Magnesium forms the compound Mg_3Bi_2 with bismuth, as noted by Grube.[2] The diagram

[1] *Zeit. anorg. Chem.*, **49**, 87 (1906).
[2] *Ibid.*, **49**, 183 (1906).

(Fig. 98) shows two branches intersecting in an eutectic point at about 18 per cent. of bismuth. The one branch has a maximum at 710° and about 40 per cent. of bismuth, which corresponds to the compound mentioned. The eutectic horizontal extends from pure magnesium to the composition of the compound, thus excluding the possibility of solid solutions being formed. The compound is very slightly

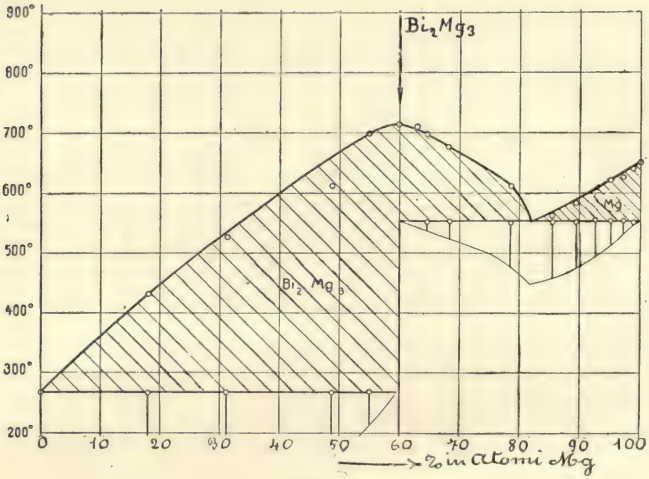

FIG. 98.

soluble in bismuth, and the eutectic alloy with bismuth consists almost entirely of bismuth. The compound is strongly exothermic. Freshly prepared it has a dark grey colour. It is very brittle ; in dry air it is stable, but in moist air it is oxidised in time to a black powder.

Magnesium-nickel.—Nickel and magnesium form, according to Voss,[1] two compounds. Mg_2Ni and $MgNi_2$. The diagram (Fig. 99) shows that at the point *D* the compound $MgNi_2$ separates from the melt. On the liquidus curve,

[1] *Zeit. anorg. Chem.*, **57**, 61 (1908).

however, instead of a maximum, a flat portion is observed. Voss maintains that along this portion of the curve crystallisation takes place from two liquid strata. He has not succeeded in demonstrating this, as hot magnesium attacks

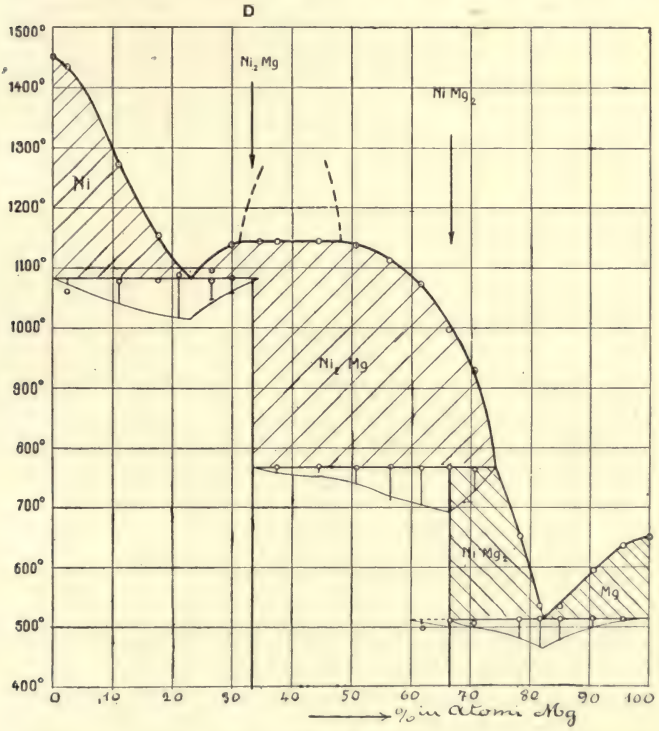

FIG. 99.

porcelain strongly with resultant perforation and loss of liquid. At 768°, $NiMg_2$ separates. On the corresponding horizontal a maximal arrest is shown for 66 per cent. magnesium.

The compound $MgNi_2$ crystallises in thin platelets. Freshly broken it has a red colour but alters quickly in the

air. The compound Mg_2Ni has not been prepared in a pure state; alloys containing it are composed of the compound $MgNi_2$ surrounded by Mg_2Ni, together with a certain quantity of the eutectic alloy.

Calcium Compounds.

Calcium-aluminium.—Donski,[1] working in Tammann's laboratory, has demonstrated the formation of the compound

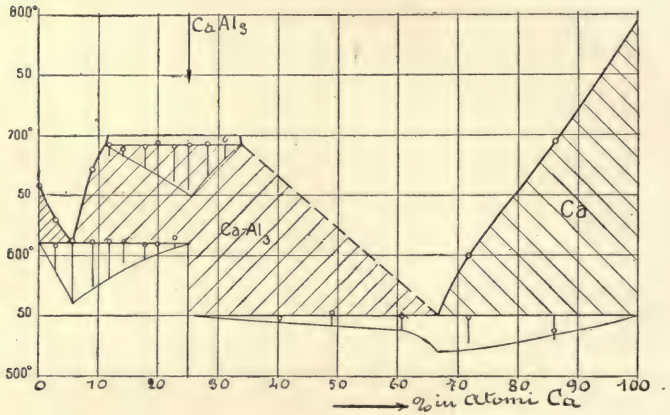

Fig. 100.

$CaAl_3$. The curve is shown in Fig. 100. Arrest points are noted at about 692° between 12 and 34 per cent. of calcium. Since two liquid strata are observed above 692°, it is supposed that they react, forming the compound $CaAl_3$ at the concentration, 25·5 per cent. of calcium, corresponding to the maximal arrest. Alloys up to 8 per cent. calcium have the colour of pure aluminium and are a little harder than this metal. They are fairly stable in air and cold water; they react with hot water giving hydrogen. Alloys with a medium calcium content are brittle, porous and show exfoliations of

[1] *Zeit. anorg. Chem.*, **57**, 185 (1908).

coarse silvery-white crystals; they decompose cold water with evolution of hydrogen.

The alloys richest in calcium are less brittle and are unstable in air.

Calcium-thallium.—Thallium and calcium combine to form the compounds $CaTl_3$, Ca_3Tl_4, and CaTl. These compounds have recently been examined thermally by Baar.[1] The preceding researches of Donski [2] are somewhat incomplete.

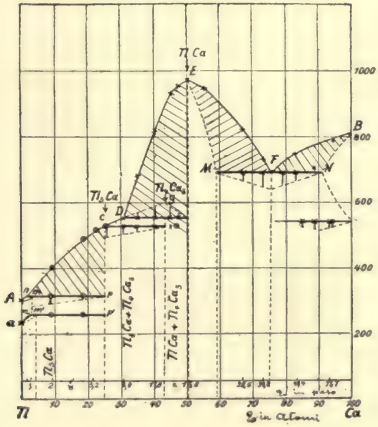

FIG. 101.

Up to 3 per cent. of calcium (see Fig. 101) a small series of mixed crystals separates; then the compound $CaTl_3$ is formed as is deduced from the prolongation of the eutectic horizontal at 310° up to the composition indicated by this formula. By addition of calcium the curve rises slowly to *D*, after which the compound Ca_3Tl_4 separates, its composition being shown by a maximal arrest at 43·7 per cent. calcium and 556°. A maximum occurs at 969° and 50·5 per cent. of calcium, corresponding to the compound CaTl. The

[1] *Zeit. anorg. Chem.*, **70**, 366 (1911).
[2] *Ibid.*, **57**, 206 (1908).

remainder of the curve indicates two series of mixed crystals between the latter compound and pure calcium.

All these alloys are unstable in air, in fact, so quickly do alloys with 55 to 85 per cent. calcium oxidise that micro-

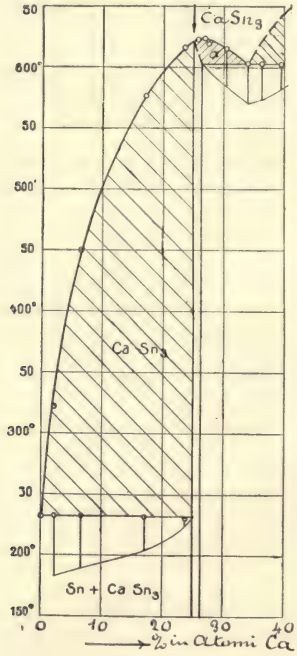

FIG. 102.

scopical examination is impossible. Alloys with 30 to 55 per cent. calcium are harder than thallium; those richest in calcium are very brittle.

Calcium-tin.—This system has been studied partially by Donski.[1] The formation of the compound $CaSn_3$ melting at 624° has been noted. The curve (Fig. 102) rises directly

[1] *Zeit. anorg. Chem.*, **57**, 206 (1908).

from the melting point of tin to the melting point of the compound. A maximum occurs at 23·7 to 26·8 per cent. of calcium and 624°. Mixed crystals are formed between 25 per cent. and 28·5 per cent. calcium containing high proportions of the compound. The alloys so far studied are oxydised in the air; those containing even as little as 2 per cent. of calcium decompose cold water with evolution of hydrogen.

Calcium-lead.—Calcium forms with lead the compounds

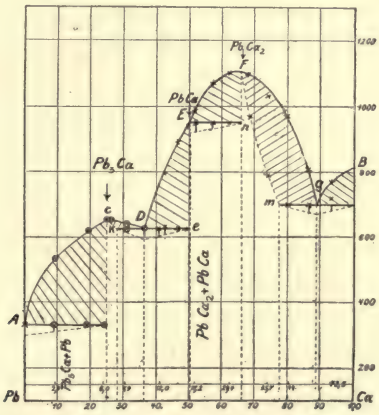

FIG. 103.

$CaPb_3$, CaPb, and Ca_2Pb. The system has been studied by Donski [1] and Baar.[2] The curve (Fig. 103) is very similar to that for calcium-tin. At 25 per cent. and 649° there is a maximum due to the compound $CaPb_3$. From the eutectic point *D* the curve rises quickly up to 982° and 51·8 per cent. calcium with separation of the compound PbCa. The curve then reaches a maximum at 1105° corresponding to the compound Ca_2Pb. From 66·6 to 89 per cent. of calcium

[1] *Zeit. anorg. Chem.*, **57**, 208 (1908).
[2] *Ibid.*, **70**, 372 (1911).

mixed crystals separate. Maximum eutectic crystallisation occurs at 89 per cent. where the resulting alloy is a conglomerate of calcium and saturated mixed crystals of calcium and the compound. These alloys are quickly oxydised in air to a black powder ; only those with 35 to 50 per cent. of calcium have been examined microscopically.

Calcium-antimony.—This system also has been studied by Donski [1] up to a concentration of 9 per cent. of calcium. The existence of a compound seems probable, but it has not been possible to define it. The investigation had to be abandoned on account of experimental difficulties, namely, the high melting point of calcium and the extreme instability of the alloys in air.

Calcium-bismuth. — Donski has also studied this system over a limited range. The formulæ of the compounds which probably occur are unknown. Arrest points have been observed between 20 and 37 per cent. of calcium at about 500°.

Compounds of Zinc.

Zinc-aluminium.—According to Tammann,[2] zinc forms with aluminium the compound Al_2Zn_3. This compound is, however, not admitted by Heycock and Neville,[3] Shepherd,[4] and Eger,[5] who have only encountered solid solutions in their investigations of the system.

Zinc-antimony.—Antimony and zinc form the compounds Sb_2Zn_3 and SbZn. The system has been investigated by Gosselin,[6] Monkmeyer,[7] and Zemczuzny.[8] The curve constructed by the latter is given in Fig. 104. There is a maximum at 566° and 60 per cent. of zinc corresponding to the

[1] *Loc. cit.*
[2] *Lehrb. d. Metall.*, p. 222.
[3] *J. C. S.*, **71**, 389 (1897).
[4] *J. Phys. Chem.*, **9**, 504 (1905).
[5] *Int. Z. f. Metall.*, **4**, 35 (1913).
[6] *Bull. Soc. d'Encour.*, (5), **1**, 1312 (1896).
[7] *Zeit. anory. Chem.*, **43**, 182 (1905).
[8] *Ibid.*, **49**, 384 (1906).

compound Sb_2Zn_3. Zemczuzny denies the existence of ZnSb, believed by Gosselin to exist. In the region corresponding to this compound, he observed marked supercooling due to the reaction $Zn_3Sb_2 + Sb = 3ZnSb$. The curve shows irregularities which, together with the formation of metastable crystals, are not observed if the liquid is seeded with crystals of ZnSb. This compound melts with decomposition, so that the curve only shows a transformation point.

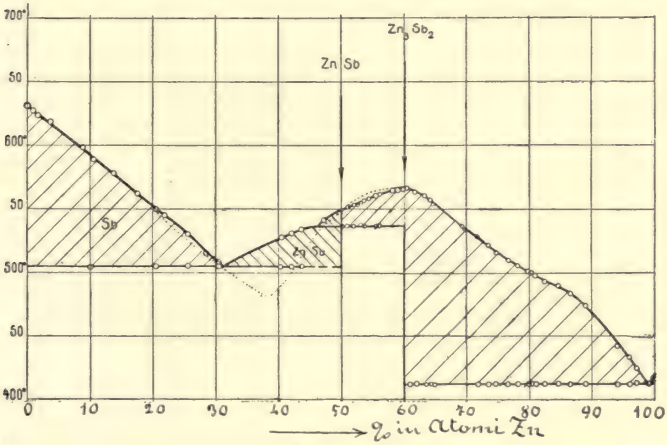

FIG. 104.

Zn_3Sb_2 shows a modification which was only observed on one side of the maximum.

Zinc-manganese.—This system has been investigated by Parravano [1] up to 29·7 per cent. of manganese. He has noted the formation of the compounds $MnZn_7$ and $MnZn_3$. The diagram is shown in Fig. 105. The melting point of zinc is lowered a few degrees by the addition of manganese, so that the first eutectic is very close to pure zinc on the diagram and only 2° below it. The two compounds are not indicated by well-defined arrests but rather by slackening in

[1] *Gazz. Chim. Ital.*, **45**, I., 1 (1915).

the cooling curves, often accompanied by super-cooling. The alloys of this system are hard and brittle.

Zinc-iron.—Iron forms with zinc the compounds Zn_7Fe and Zn_3Fe. There are also three series of mixed crystals. The system has been studied by Wologdine,[1] Guertler,[2] von Vegesack[3] and finally by Raydt and Tammann.[4] The diagram (Fig. 106) is that of von Vegesack, completed by

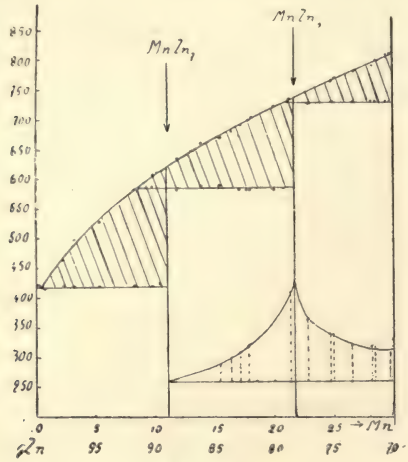

FIG. 105.

Raydt and Tammann. At 777° and 25 per cent. of iron the melt separates the compound Zn_3Fe which undergoes a transformation to the compound Zn_7Fe at 662° and 15 per cent. iron. As above mentioned there are three species of mixed crystals, one up to ·7 per cent. of iron, the second from 7·3 to 11 per cent. of iron, and the third from 80 to 100 per cent. of iron. From 25 to 86 per cent., the alloys consist of

[1] *Rev. d. Métall.*, **3**, 701 (1906).
[2] *Int. Z. f. Metall.*, I., 355.
[3] *Zeit. anorg. Chem.*, **52**, 36 (1907).
[4] *Ibid.*, **83**, 257 (1913).

saturated mixed crystals and the compound Zn_3Fe; from 25 to 15 per cent., of the two compounds Zn_3Fe and Zn_7Fe and from 7·3 to ·7 per cent., of the two saturated mixed crystals.

Magnetic properties are observed in alloys from 26·2 to 96 per cent. of iron; such properties diminish in intensity with decrease of iron content. The alloys with 11 to 22 per

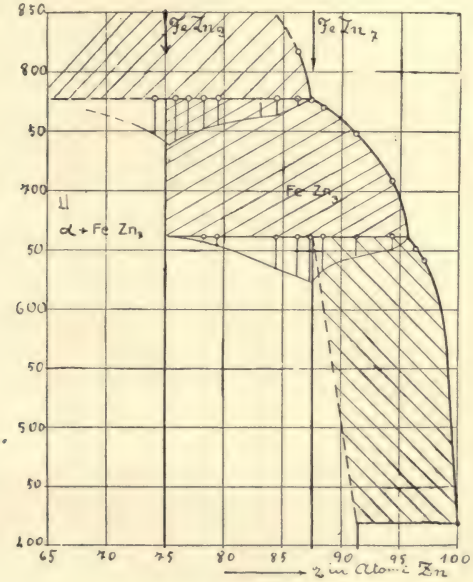

FIG. 106.

cent. of iron containing the two compounds are exceptional. Probably their properties are due to the presence of small quantities of iron. On heating, such alloys lose their magnetic properties. The iron-zinc alloys are porous, hard, and very brittle.

Zinc-cobalt.—This system has been studied by Levkonja [1]

[1] *Zeit. anorg. Chem.*, **59**, 319 (1908).

to a limited degree, and, up to the present, the only compound recognised is one having the formula $CoZn_4$. The maximum corresponding to this compound occurs at about 880° and 18·5 per cent. by weight of cobalt (see Fig. 107). From 5 to 13·4 per cent. of cobalt mixed crystals are formed.

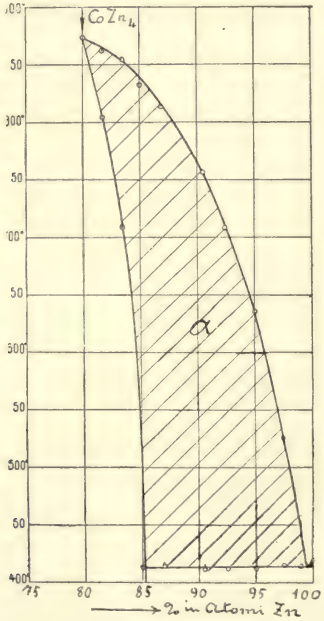

FIG. 107.

From the melts of alloys containing 5 to 13·4 per cent. cobalt, there are separated, primarily, unsaturated mixed crystals which by addition of zinc pass, on cooling to 419°, to the saturated mixed crystals *a*. Levkonja has not observed magnetic properties in the alloys containing up to 18·4 per cent. of cobalt.

Zinc-nickel. — Nickel forms with zinc the compound

Zn_3Ni and ZnNi, according to Tammann [1] and Voss.[2] The diagram constructed by the latter is given in Fig. 108. The melting point of zinc is not lowered by addition of nickel, and the curve rises directly from the zinc axis. Between 14·5 and 23 per cent. of nickel a distinct interval occurs,

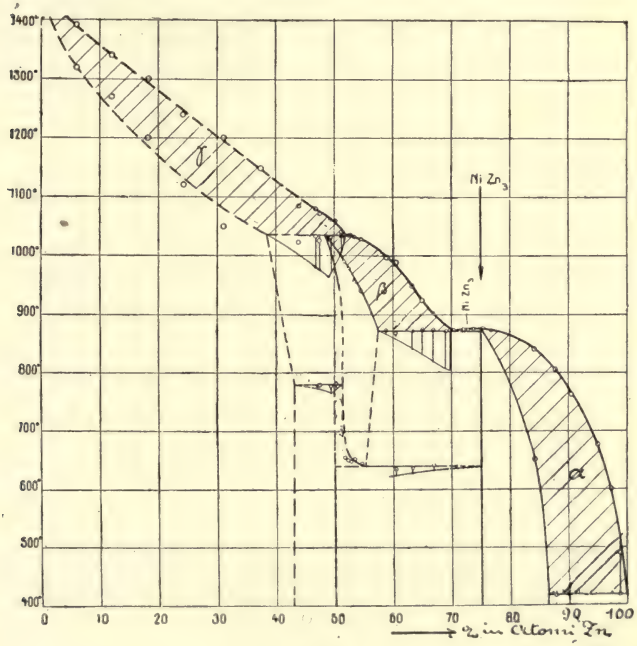

FIG. 108.

together with a point of discontinuity. This range corresponds to the mixed crystals formed between Zn_3Ni and Zn, the saturated mixed crystal occurring at 14·5 per cent. nickel.

Microscopical examination confirms the results of thermal analysis.

[1] *Métallurgie*, **4**, 781 (1907).
[2] *Zeit. anorg. Chem.*, **57**, 67 (1908).

Cadmium Compounds.

Cadmium-tin. — Information on this system is as yet incomplete ; the compound $CdSn_4$ is probably formed. The system has been investigated by Kapp [1] and Stoffel,[2] and the diagram is shown in Fig. 109. Stoffel studied the alloys not only by thermal but also by microscopical and dilatometric methods ; he also made determinations of electromotive force. The last method, for some unknown reason, gave negative results, while the microscopical results were uncertain. He found a thermal arrest at 122° for all alloy

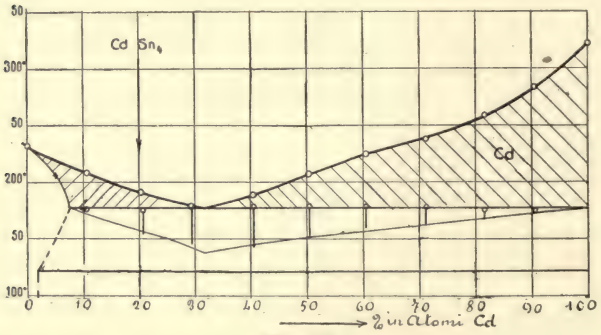

Fig. 109.

from 2·5 to 50 per cent. of cadmium and accompanying small changes of volume, of which, however, he was unable to note the maximum.

Cadmium-antimony.—Antimony and cadmium form well-defined compounds, namely, CdSb and Cd_3Sb_2, the latter of which is in accordance with the known valencies of the two metals. The results obtained by Treitschke [3] and Kurnakoff and Konstantinoff [4] are in fair agreement. The diagram (Fig. 110) shows a maximum at 455° and 50 per cent. An eutectic horizontal at 290° reaches to a point below the

[1] *Ann. d. Phys.*, **6**, 754 (1901).
[2] *Zeit. anorg. Chem.*, **53**, 140 (1907).
[3] *Ibid.*, **50**, 217 (1906).
[4] *Ibid.*, **58**, 12 (1908).

maximum of the liquidus curve. Between 36 and 51·6 per cent. of antimony the compound CdSb separates as a solid phase of constant composition. By very slow cooling, another line (shown in dots on the diagram) is obtained, which corresponds to Cd_3Sb_2, with a maximum at 423°. The cooling curves in this region show the formation of solid solutions. At 260 to 290° a reaction takes place in the solid

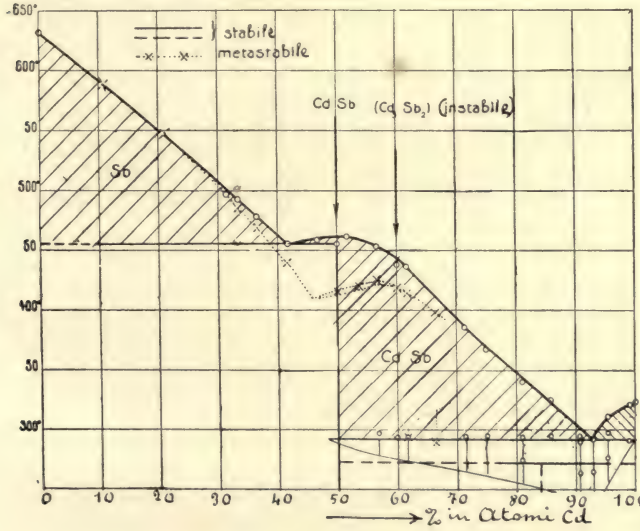

FIG. 110.

state with a rise of temperature of 20 to 30 degrees. This evolution of heat reaches a maximum for alloys containing 50 per cent. of antimony. The transformation is, of course, that of Cd_3Sb_2, which is unstable, into CdSb, which is stable, and has a higher melting point ($Cd_3Sb_2 + Sb = 3CdSb$). The transformation point corresponding to stable Cd_3Sb_2 is at 409° and 66·5 per cent. of cadmium.

Cadmium-chromium. — Hindrichs[1] in a study of this

[1] *Zeit. anorg. Chem.*, **59**, 427 (1908).

system did not succeed in obtaining positive results and our information is incomplete.

Cadmium-iron.—The degree of chemical combination between cadmium and iron is not as yet completely known. The system has been investigated by Isaac and Tammann,[1] who found that on adding iron dust to molten cadmium and heating for a long time at 650° only one arrest point was obtained, which was in fact identical with the melting point of cadmium (321°). Microscopical analysis revealed the presence of conglomerates, which Isaac and Tammann believe to contain a compound of the two metals. It is doubtful whether any compound rich in cadmium exists (as in the case of iron and zinc) or whether such compound is practically insoluble at its melting point. If such were the case a single arrest would be noted at the melting point of cadmium, which actually occurs.

Cadmium-cobalt.—In this case also it is doubtful whether compounds are formed. The system has been studied by Levkonja,[2] who found an eutectic crystallisation in alloys with 2·5 to 10 per cent. cobalt at 316° to 6° below the melting point of pure cadmium. It was not possible to ascertain whether chemical combination took place.

The alloys obtained did not exhibit magnetic properties at ordinary temperatures.

Cadmium-nickel.—Nickel and cadmium combine to form the compound Cd_4Ni. The system has been studied, though to a limited extent, by Voss,[3] whose observations do not extend below 15 per cent. on account of the volatility of cadmium. An eutectic horizontal at 321° extends from 20 per cent. of nickel, the composition of the compound, to pure cadmium (see Fig. 111). Another horizontal is shown at 405° whose nature is not exactly understood. It evidently indicates a new species of mixed crystals. The nature of the solid phase above 502° is not known.

[1] *Zeit. anorg. Chem.*, **55**, 61 (1907).
[2] *Ibid.*, **59**, 322 (1908).
[3] *Ibid.*, **57**, 69 (1908).

Compounds of Mercury (Amalgams).

The amalgams are of considerable historical importance in the study of the solubility of metals. It may be mentioned that Ramsay and Tammann used mercury as a solvent in their studies on the atomicity of metallic molecules by the cryoscopic method. Our knowledge of the chemical compounds of mercury with other metals, although abundant, is somewhat inexact, as only in a few instances has the thermal method been used to ascertain formulæ. We shall, how-

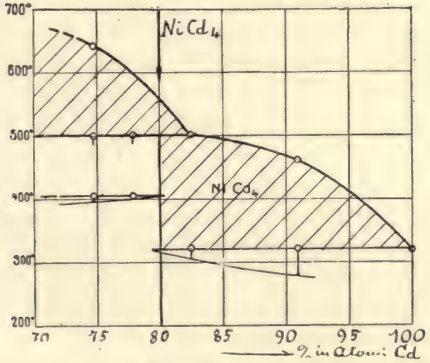

Fig. 111.

ever, not confine our description to the amalgams studied by the thermal methods which have so much enlarged the field of scientific investigation. A reliable summary of our knowledge of the various amalgams studied by the older methods of chemistry has been made by Ley.[1] We shall now allude briefly to the information which we actually possess of the crystalline amalgams.

Mercury-aluminium. — The aluminium amalgams have received considerable attention, but at present little is known of the capacity for chemical combination between the two metals.

[1] *Cf. Handbuch d. anorg. Chem.*, R. Abegg, Vol. II., pp. 569 *et seq.*

Cossa [1] prepared an amalgam by fusion in an atmosphere of inert gas; Tarugi [2] allowed mercury vapour to act on aluminium.

The compound Hg_3Al_2 is supposed to exist, but this is not certain. Aluminium amalgam is chemically very reactive.[3]

Mercury-gallium.—This system has not yet received any attention. Ramsay [4] states that gallium dissolves easily in mercury, in which it agrees with thallium. It is, therefore, not improbable that the two metals combine chemically.

Mercury-indium.—T. W. Richards and Wilson [5] studied the electro-chemical potential of indium amalgams, and obtained values in excess of those calculated by the mixture rule. According to Hildebrand [6] the compound Hg_4In can probably occur.

Mercury-thallium.—This system has been studied by Kurnakoff and Pushin,[7] who noted the existence of the compound Hg_2Tl. Studies have also been made by Regnault [8] and Carstanjen,[9] the former of whom affirmed the existence of the compounds Hg_5Tl_2 and Hg_1Tl_2. The most recent investigations are those of Paulovitch,[10] who has confirmed the work of Kurnakoff and Pushin and added some considerations on irrational dystectics.

The behaviour of thallium with mercury resembles to an extent that of the alkali metals which give the type RHg_2. The diagram of Kurnakoff and Pushin (Fig. 112) gives a maximum at 15° and 33·3 per cent. of thallium. The branch

[1] *Nuovo Cimento*, (2), **3**, 75 (1870).
[2] *Gazz. Chim. Ital.*, **34**, II., 486 (1904).
[3] *Cf.* Tissier, *C. R.*, **49**, 54 (1859); Casamajor, *Chem. News*, **34**, 34 (1876); Jehn, *Ber.*, **11**, 360 (1878); Kronchkoll, *J. de Phys.*, (2), **3**, 139 (1884); Ramsay, *J. C. S.*, **55**, 521 (1889); Schumann, *Wied. Ann.*, **43**, 101 (1891); Coehn and Ormandy, *Ber.*, **28**, 1505 (1895); Biernacki, *Wied. Ann.*, **59**, 664 (1896); Humphreys, *J. C. S.*, **69**, 1679 (1896); Konovaloff, *Chem. Centr.*, 1896, II., p. 338; Richards, *Chem. News*, **74**, 30 (1896).
[4] *J. C. S.*, **55**, 553 (1889).
[5] *Zeit. phys. Chem.*, **72**, 141, 157, 164 (1910).
[6] *J. Amer. C. S.*, **35**, 513 (1913).
[7] *Zeit. anorg. Chem.*, **30**, 104 (1902).
[8] *C. R.*, **64**, 111 (1867).
[9] *J. prakt. Chem.*, **102**, 84 (1867).
[10] *Journ. Russ. phys.-chem. Soc.*, **47**, 29—46 (1915); *Bull. Soc. Chim.*, (4), **20**, 2 (1916).

of the curve on which this maximum occurs belongs therefore to the compound $TlHg_2$ which melts without decomposition. Along the branch α, liquid amalgams separate. At low temperatures thallium is very soluble in mercury and lowers the freezing point of the latter to − 60°, which is the temperature

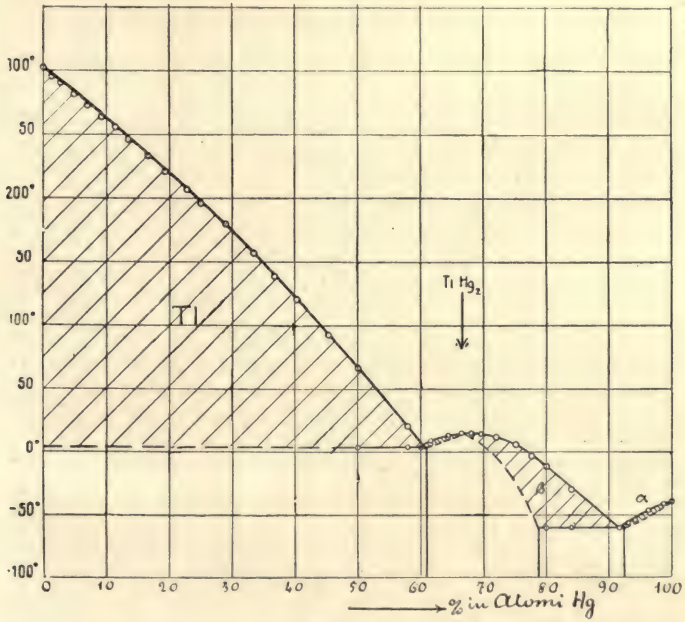

FIG. 112.

of eutectic solidification. It may be added that this is the lowest freezing point hitherto observed for any alloy.

Mercury-tin.—Tin dissolves in mercury, even at ordinary temperatures, with evolution of heat. According to Roozeboom [1] and Van Heteren,[2] tin and mercury form solid solutions. Pushin [3] has also noticed the formation of solid

[1] *Verh. K. Ak. Wetensch.*, Amsterdam, 420 (1902).
[2] *Zeit. anorg. Chem.*, **42**, 129 (1904).
[3] *Ibid.*, **36**, 207 (1903).

solutions. Kupffer [1] and Matthiessen [2] have determined the specific gravity of these amalgams. Tammann [3] studied the effect of the addition of small quantities of tin on the freezing point of mercury. He found that the freezing point was raised as follows :—

·063	gram. Sn	dissolved	in 100 gm.	Hg raised the f.p.	·06°
·148	„	„	„	„	1·1°
·219	„	„	„	„	2·1°
·281	„	„	„	„	2·4°

According to Tammann the existence of the compound Hg_3Sn is probable, but the actual data render more probable the existence simply of isomorphous mixtures of the two metals.

Mercury-cerium.—The solubility of cerium in mercury was observed by Winkler,[4] and by Muthmann and Beck.[5] Cerium is very soluble in boiling mercury. Nothing is known of the capacity for combination of these metals.

Mercury-antimony.—Mercury is without action on antimony in the cold ; an amalgam is formed at higher temperatures. Amalgams of mercury have been prepared by means of the usual indirect methods by Böttger [6] and Vortmann.[7] According to Partheil and Mannheim,[8] the compound Hg_3Sb_2 is probably formed.

Mercury-uranium.—The amalgams of uranium, prepared electrolytically by Férée,[9] lose mercury on heating to 242°, leaving a residue of uranium which ignites spontaneously.

Mercury-chromium. — Chromium amalgams have been prepared by the direct fusion of the two elements. Schönbein [10] and Vincent [11] obtained them by acting upon sodium

[1] *Ann. Chem.*, **40**, 293.
[2] *Pogg. Ann.*, **112**, 445.
[3] *Zeit. phys. Chem.*, **3**, 441 (1889).
[4] *Ber.*, **24**, 1883 (1891).
[5] *Ann. Chem.*, **331**, 56 (1904).
[6] *J. prakt. Chem.*, **12**, 350 (1837).
[7] *Ber.*, **24**, 2762 (1891).
[8] *Arch. Pharm.*, **238**, 160 (1900).
[9] *Bull. Soc. Chim.*, (3), **25**, 622 (1901).
[10] *Jahresber.*, 1861, p. 95.
[11] *Phil. Mag.*, (4), **24**, 328 (1862).

and potassium amalgams with concentrated chromium chloride solution. They have also been prepared and studied by Moissan. [1]

Myers [2] and Férée [3] obtained chromium amalgams by electrolysis of chromium sulphate solution with a mercury cathode.

The compounds Hg_3Cr and HgCr have been described in chemical literature. The compound Hg_3Cr loses mercury easily under pressure giving the other hypothetical compound HgCr. This in its turn loses mercury on heating to 300°, leaving a residue of chromium (Férée).

It is probable that these metals form solid solutions rather than definite compounds.

Mercury-molybdenum. — The amalgams of molybdenum have been prepared by electrolysis of a solution of molybdic anhydride in hydrochloric [4] or sulphuric [5] acid. Férée [6] obtained a semi-solid amalgam by electrolysis: from the crystalline phase, the compounds Hg_9Mo, Hg_2Mo, and Hg_3Mo_2 separated under pressure. These compounds, however, lose their mercury completely on heating, leaving behind a residue of pyrophoric molybdenum.

Mercury-manganese. — Manganese amalgams have been prepared by Böttger,[7] Giles,[8] Moissan,[9] and J. Schumann,[10] by the action of sodium amalgam on manganous chloride. Ramsay [11] obtained an amalgam by electrolysis of manganese chloride solution using a mercury cathode. The researches of O. Prelinger [12] must also be mentioned; from these the existence of the compound Mn_2Hg_5 is argued.

[1] *C. R.*, **88**, 180 (1879); *Ann. Chim. Phys.*, (5), **21**, 250 (1880).
[2] *J. Am. C. S.*, **26**, 1126 (1904).
[3] *C. R.*, **121**, 823 (1895).
[4] *Zeit. Elektroch.*, **12**, 146, 154 (1906).
[5] *J. Am. C. S.*, **26**, 1124 (1904).
[6] *C. R.*, **122**, 733 (1896).
[7] *J. prakt. Chem.*, **12**, 350 (1837)
[8] *Phil. Mag.*, (4), **24**, 328 (1862).
[9] *C. R.*, **86**, 180 (1879).
[10] *Wied. Ann.*, **43**, 110 (1891).
[11] *J. C. S.*, **55**, 532 (1889).
[12] *Ber. Wien. Akad.*, **102**, 346 (1893).

Mercury-iron.—These amalgams have been prepared exclusively by indirect methods, either electrolytically, or else by the action of alkali amalgams on solutions of iron salts. Cailletet [1] showed that iron may be superficially amalgamated. From amalgams containing about 15 per cent. of iron Joule [2] obtained, by the application of pressure, a crystalline phase of composition FeHg. Zamboni [3] prepared an iron amalgam by electrolysis of ferrous ammonium sulphate, using a mercury cathode, Rammann, [4] by the same method as Joule obtained a solid phase of composition Fe_2Hg_3. It is not, however, certain whether mercury and iron combine chemically.

Mercury-cobalt and *mercury-nickel.* — These amalgams have been little studied with reference to the capacity of their components for chemical combination. They have been prepared by Darmour,[5] Moissan [6] and Schumann.[7]

Mercury-platinum, etc.—Little is known of the amalgams of platinum, palladium, osmium, iridium, rhodium and ruthenium. Joule [8] obtained a crystalline amalgam of platinum of composition $PtHg_{12}$. It is most probable that these metals form simple isomorphous mixtures with mercury.

Compounds of Metals of Group III. with Metals of other Groups.

Compounds of Aluminium.

Aluminium-cerium.—The system has been investigated by Vogel,[9] who claims that five compounds are formed, namely, $AlCe_3$, $AlCe_2$, AlCe, Al_2Ce, and Al_4Ce. Two of these com-

[1] *C. R.*, **44**, 1250 (1857).
[2] *J. C. S.*, (2), **1**, 378 (1863).
[3] *Nuovo Cimento*, (4), **2**, 26 (1895).
[4] *Ber.*, **14**, 1433 (1881).
[5] *J. prakt. Chem.*, **17**, 346 (1839).
[6] *C. R.*, **88**, 180 (1870).
[7] *Wied. Ann.*, **43**, 111 (1891).
[8] *Jahresber.*, 1850, p. 333; 1863, p. 280.
[9] *Zeit. anorg. Chem.*, **75**, 41 (1912).

pounds, Al_2Ce and Al_4Ce, have melting points much above those of their components. The curve (Fig. 113) shows two maxima, one very pronounced at about 1460° and 33 per cent. of cerium due to the compound $CeAl_2$, and the other, not so pronounced, at about 614°, corresponding to Ce_3Al. The asymmetry of the latter maximum is due in all probability to the compound Ce_3Al being strongly dissociated, while the

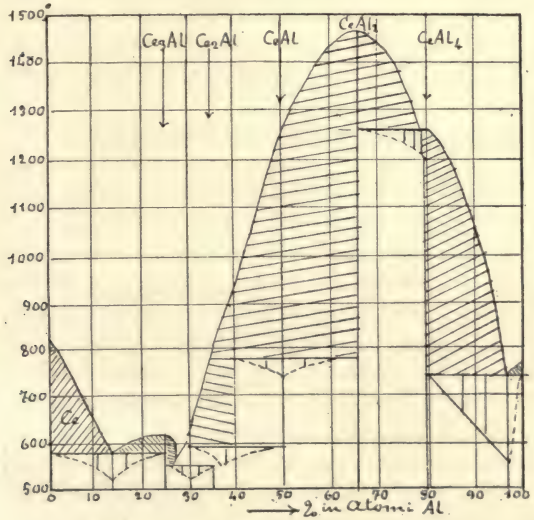

FIG. 113.

compound Ce_2Al is less disscciated. The latter compound, formed at 33 per cent. of aluminium, melts at 595° with decomposition into CeAl and a melt; CeAl separates primarily in beautiful prisms which at 780° split up into $CeAl_2$ and a fused mixture. Above 700°, between 35 and 50 per cent. of aluminium, weak thermal effects are noted which may be due to the occurrence of lanthanium and didymium in the cerium used for experiment. After $CeAl_2$, which separates at about 67 per cent. of aluminium, comes the compound Al_4Ce which

separates at 1245° and 80 per cent. of aluminium. This compound undergoes a polymorphic transformation at 1005° which is shown in the diagram as a weak thermal effect. The change from the form β, stable at higher temperatures, to the form α, stable at lower temperatures, is characterised by a contraction.

The cerium-aluminium alloys are in general stable in the air, unacted upon by water, and more resistant to the action of acids than the pure metals. They exhibit distinct hardness between 35 and 80 per cent. of aluminium with a maximum for $CeAl_2$. With this hardness is associated extreme brittleness.

Aluminium-antimony.—The various chemical combinations of these metals, if indeed they exist, have not been well elucidated up to the present. The existence of a compound AlSb seems certain. Wright [1] noted that antimony and aluminium form an alloy with a high melting point, and containing 81·6 per cent. by weight of antimony (corresponding to AlSb). Roche [2] and Gautier [3] have confirmed this result. The study of the equilibrium system is due to Campbell and Matthews [4] and, later, to Tammann.[5]

The fusion diagram (Fig. 114) shows two maxima, one at 50 to 53 per cent. of aluminium and the other at 90 per cent. aluminium. Of these, the former corresponds to the compound AlSb ; no crystalline species has been found to correspond to the latter maximum. Tammann has attempted to solve this problem by showing that the form of the curve is different when this single compound of aluminium and antimony is formed slowly from its fused components. If the compound is formed more quickly there may occur a displacement of the maximum, an increase of the quantity of one of the components, or even the appearance of a second

[1] *J. C. S. I.*, 1892, p. 493.
[2] *Mon. Scient.*, (4), **7**, 269 (1893).
[3] *Bull. Soc. d'Encour.*, (5), **1**, (1896).
[4] *J. Am. C. S.*, **241**, 259 (1902).
[5] *Zeit. anorg. Chem.*, **48**, 53 (1906).

maximum. The compound AlSb is formed slowly from its components at about 700° ; at 1100° the reaction proceeds very rapidly. (*Cf.* p. 7).

Aluminium-manganese.—Two compounds of these metals with each other occur, but their composition has not been ascertained with certainty up to the present. According to Gwyer,[1] their formulæ are probably $AlMn_3$ and Al_3Mn, respectively. Guillet [2] prepared alloys of aluminium and

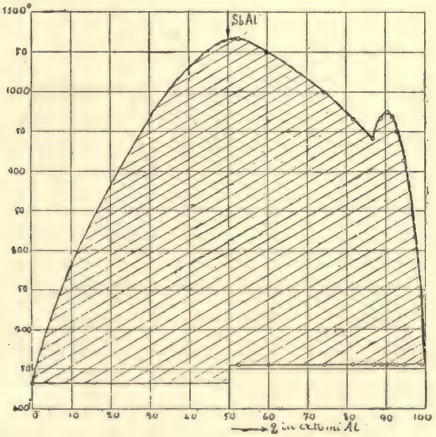

FIG. 114.

manganese and found the compounds Al_3Mn, Al_3Mn_2 and Al_4Mn.

Hindrichs [3] has studied the system by means of thermal methods The diagram (Fig. 115) shows that the melting point of manganese is raised by addition of aluminium. At about 90 per cent. of manganese there occurs, at 1279°, the first separation. Between 10 and 35 per cent. of aluminium the temperature only changes by about 2°. Further, on the cooling curves of melts from 5 to 40 per cent. of aluminium,

[1] *Zeit. anorg. Chem.*, **57**, 150 (1908).
[2] *C. R.*, **134**, 236 (1908) ; *Le Génie Civil*, **41**, 139, 156, 169, 188, 363, 377, 393 (1902).
[3] *Zeit. anorg. Chem.*, **59**, 44 (1908).

distinct crystallisation intervals occur with a minimum at 14 per cent. of aluminium. The temperature change of 2° on the fusion curve may well be due to ordinary experimental error, for the temperature along that portion of the curve should either remain constant or else show a maximum. In

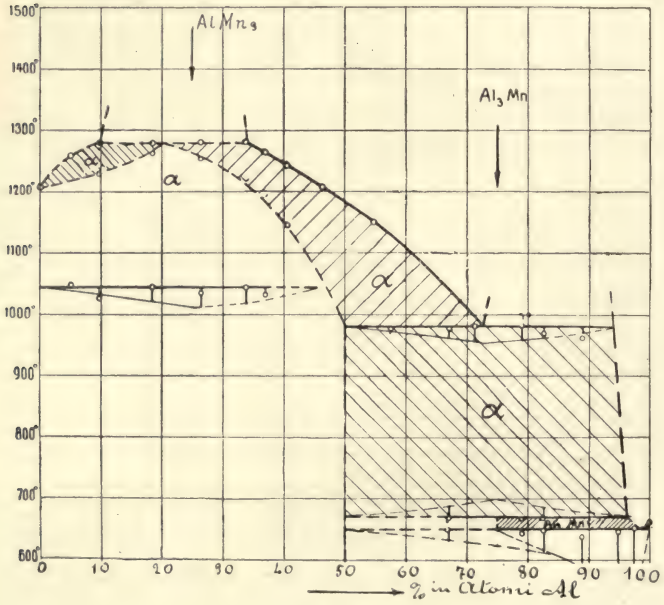

FIG. 115.

the former case a compound would be formed from the melts in question, in the latter case there would occur a crystallisation of a series of homogeneous melts into a continuous series of mixed crystals, of which that mixed crystal with the highest melting point would be a definite compound. Thermal analysis does not enable us to decide which is actually the case that occurs. At 1040° to 1050° small arrests are noted in the alloys up to 45 per cent. of aluminium with a

maximal arrest at about 27 per cent. which should be due to the decomposition of mixed crystals with 50 per cent. of aluminium into manganese and the crystals α. If the mixed crystals formed from the melt consist of the compound $AlMn_3$ there ought here to be a decomposition of $AlMn_3$ into manganese and the mixed crystals α. From 35 to 73 per cent. mixed crystals separate. Between 73 and 95 per cent. there exists a gap in miscibility. The formation of mixed crystals is accompanied by super-cooling. At 670° the melt α reacts with the saturated mixed crystals forming a compound which may be detected by microscopical examination. Its formula is probably Al_3Mn.

Aluminium-iron.—Gwyer [1] states that these metals form a compound Al_3Fe. Between 100 and 43 per cent. of iron (see Fig. 116) a series of mixed crystals is formed. From 30 to 50 per cent. of iron there occur on the cooling curve either breaks due to primary separation or else eutectic arrest points; these occur at 1087° for alloys with 65, 62·5 and 60 per cent. of aluminium, and at higher temperatures for alloys between 57·5 and 50 per cent. of aluminium. From 67·5 to 76·8 per cent. aluminium, crystallisation intervals are noted which correspond to a series of mixed crystals of which the last member, at about 75 per cent., probably represents the compound $FeAl_3$. In the alloys from 41 to 0 per cent. of iron the proportion of $FeAl_3$ diminishes, while that of aluminium increases. In the cooling of these alloys a very small thermal effect is observed at 550°, believed by Gwyer to be due to the formation of a compound from Al_3Fe and Al; this compound is, however, not detected by microscopical analysis.

The reaction between the two metals is accompanied by such an evolution of heat that Gwyer was unable to make use of porcelain fusion tubes and was obliged to substitute tubes of magnesia.

Aluminium-cobalt.—These metals combine, forming the

[1] *Zeit. anorg. Chem.*, **57**, 129 (1908).

compounds Co_3Al_{13}, Co_2Al_5 and CoAl. This system also was studied by Gwyer.[1] The curve (Fig. 117) is somewhat similar to that for FeAl. It shows two discontinuities and a maximum. Between 100 and 80 per cent. cobalt mixed crystals of the two metals are formed. From 80 to 50 per

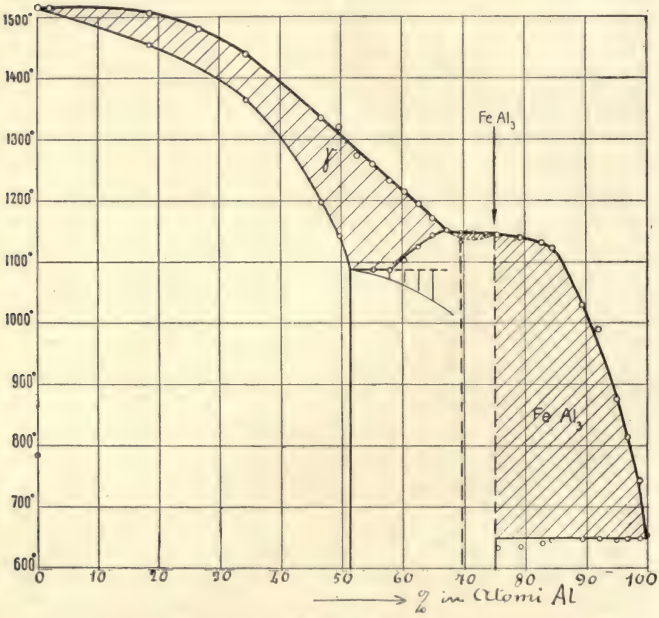

FIG. 116.

cent. all cooling curves show crystallisation intervals, but microscopical analysis shows that only those alloys with 50 to 65 per cent. cobalt have a homogeneous structure, while from 80 to 65 per cent. two structural elements are observed. Since these alloys even on long annealing do not acquire homogeneity, Gwyer concludes that there is here an

[1] *Zeit. anorg. Chem.*, **57**, 136 (1908).

interrupted series of mixed crystals (with a maximum) or else a gap in miscibility between two phases. At 1628° and 50 per cent. the compound CoAl crystallises. The latter, reacting with the melt, gives at 1165° and 22·5 per cent. of

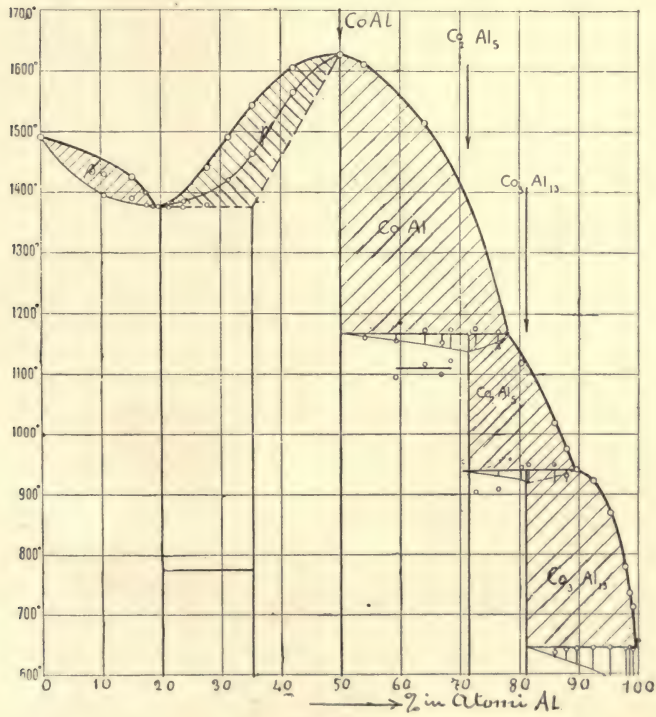

FIG. 117.

cobalt, the compound Co_2Al_5. At 1110° small breaks are noted which probably indicate a polymorphic transformation. From Co_2Al_5 and the melt, crystals of Co_3Al_{13} separate at 940° and 18 per cent. cobalt. The formulæ of the last two compounds are indicated by the positions of the maximal arrests.

Gwyer observed very small thermal effects also at 550° ; he believes it possible that there are two such effects, one for a reaction between Co_3Al_{13} and aluminium, and the other in alloys richer in Co_3Al_{13} due to a polymorphic transformation in this compound.

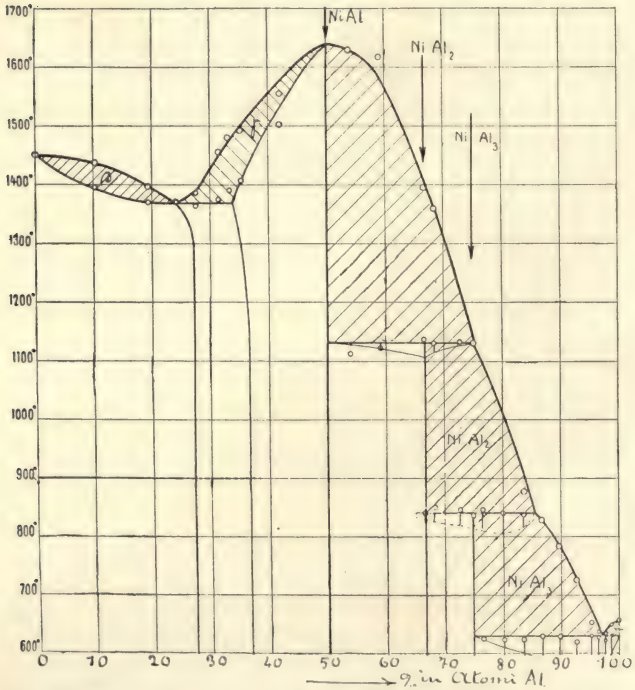

FIG. 118.

Aluminium-nickel.—These metals form the following compounds : $NiAl_3$, $NiAl_2$ and NiAl. The system was studied by Gwyer (*loc. cit.*). The curve (Fig. 118) shows a maximum, two discontinuities and an eutectic point. Between 100

and 73·15 per cent. of nickel there separates a series of mixed crystals of the two metals. From 63 to 73·5 per cent. small arrests are noted at 1370°; these alloys consist of two species of crystals. At lower temperatures, however, this lack of miscibility changes; in fact the alloy with 63 per cent. of nickel after long annealing has a homogeneous structure. From 73 to 50 per cent. of nickel there is a series of mixed crystals of NiAl and nickel. The maximum shows that at about 1640° and 50 per cent., the compound NiAl is formed. At 1130°, by action of the melt containing 25 per cent. nickel on the crystals of NiAl, the compound $NiAl_2$ is formed at a concentration of 34 per cent. These crystals of primary separation react at 825° with a melt containing 15 per cent. nickel, forming at 25 per cent. a compound which is probably $NiAl_3$.

Aluminium-chromium.—The compound $AlCr_2$ is probably formed from these two metals. The system was studied by Hindrichs [1] to a limited extent. Working with alloys containing more than 70 per cent. of aluminium, the temperature of fusion was so high that the aluminium attacked and destroyed the magnesia tubes which were used. It was, therefore, necessary to study these alloys by micrographical methods alone. At 644° (see Fig. 119) arrests were noted as far as 60 per cent. of chromium. By extrapolation it would appear that they die out at 85 per cent. chromium. From 5 to 70 per cent. there are also arrests at 975°. The separation which occurs here is often accompanied by slight supercooling. On the higher branch of the curve there probably occurs the separation of compound with a very high melting point. Microscopical examination shows that alloys from 85 to 96 per cent. of aluminium have a homogeneous structure; they represent mixed crystals of chromium and a compound of the two metals. The formula is probably $AlCr_3$, which would require 85·12 per cent. by weight of chromium.

[1] *Zeit. anorg. Chem.*, **59**, 433 (1908).

Thallium Compounds.

Thallium-lead.—With thallium, lead probably forms the compound $PbTl^1$. The system has been studied by Levkonja [1] and by Kurnakoff and Pushin.[2] It is of interest by reason of certain considerations which may be made with

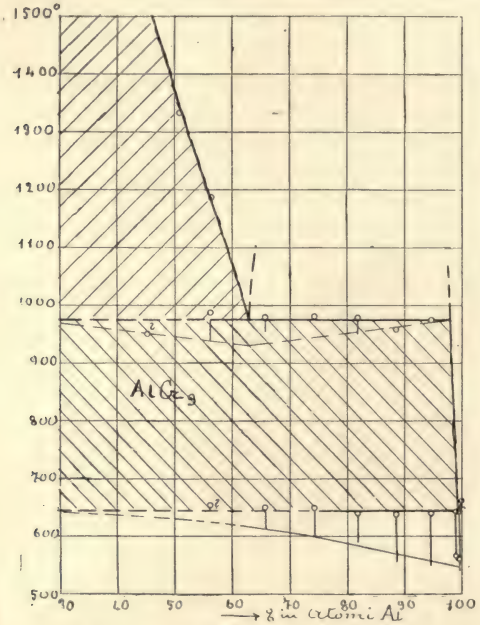

Fig. 119.

reference to the application of thermal analysis to the interpretation of equilibrium diagrams. Each metal raises the melting point of the other, and the fusion curve passes through a point representing a much higher temperature than either of the melting points of the pure metals.

[1] *Zeit. anorg. Chem.*, **52**, 454 (1907).

[2] *Ibid.*, p. 435. L. Rolla studied the thermo-electric power and specific volume of these alloys. *Gazz. Chim. Ital.*, **45**, I., 185 (1915).

Levkonja holds that this maximum (see Fig. 120) which occurs at about 275° and 34 per cent. of lead indicates the compound $PbTl_2$ which forms solid solutions with both components. Kurnakoff and Pushin, however, contend that the curve merely indicates the formation of solid solutions and belongs to Roozeboom's second type (see p. 16). This question can only be resolved by microscopical examination. Kurnakoff has, however, given powerful support to his contention by observing that the addition of tin displaces

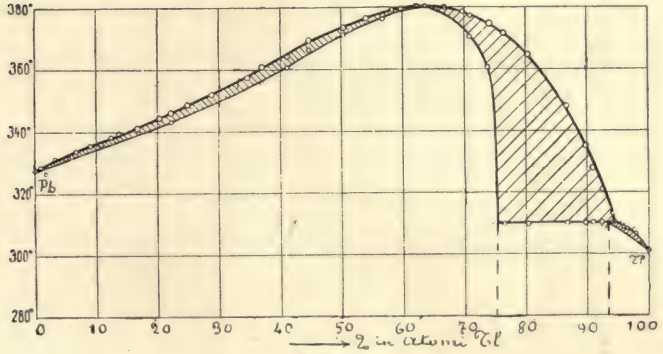

FIG. 120.

the maximum to a point where Tl : Pb = 1 : 2·5 instead of 1·7 — 1·8 : 1.

Thallium-antimony.—Antimony and thallium combine to form the compound $SbTl_3$. The system has been investigated by Williams[1] (see Fig. 121). Pure antimony crystallises from melts rich in that metal. Thallium occurs in two polymorphic forms which transform at 225°. From melts between 29·8 and 22 per cent. of antimony, pure thallium does not separate, but a series of mixed crystals. At 195° conglomerates are formed which consist of antimony and mixed crystals of α Tl with 22 per cent. of antimony ; from 22 to 0 per cent. they consist of a series of mixed crystals of

[1] *Zeit. anorg. Chem.*, **50**, 129 (1906).

composition corresponding to that of the melt. At 187° or 8° below the eutectic temperature and 25 per cent. of antimony a new species of crystals is formed, namely, the compound $SbTl_3$, with a super-cooling of about 2°.

Alloys with less than 50 per cent. of thallium are hard, brittle and capable of receiving a polish. With increase of thallium they become softer and can only be polished with difficulty.

Microscopical analysis has confirmed these results,

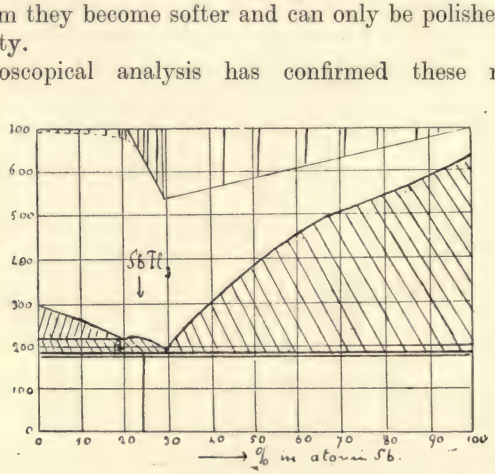

FIG. 121.

although at 187° Williams failed to obtain a homogeneous alloy, for there occurred an admixture of rod-like crystals of antimony. On subjecting this heterogeneous alloy to prolonged annealing, however, the free antimony diminished in amount and finally almost disappeared. At 22 per cent. the quantity of the compound decreased while that of the mixed crystals α TlSb increased.

Thallium-bismuth.—This system is of particular interest. The two metals combine but, as was mentioned in a preceding chapter, their combination cannot be reconciled with the law of definite proportions. Chikashigé [1] first studied the system

[1] *Zeit. anorg. Chem.*, **51**, 330 (1906).

which was subsequently examined by Kurnakoff, Zemczuzny and Tararin.[1] The fusion diagram shows three maxima, two of which are distinct and one less pronounced. The first of these maxima occurs at ·9 per cent. of bismuth at 301·5°; it corresponds to the separation of a solid solution of bismuth in thallium (phase β). At 5·8 per cent. these solid solutions

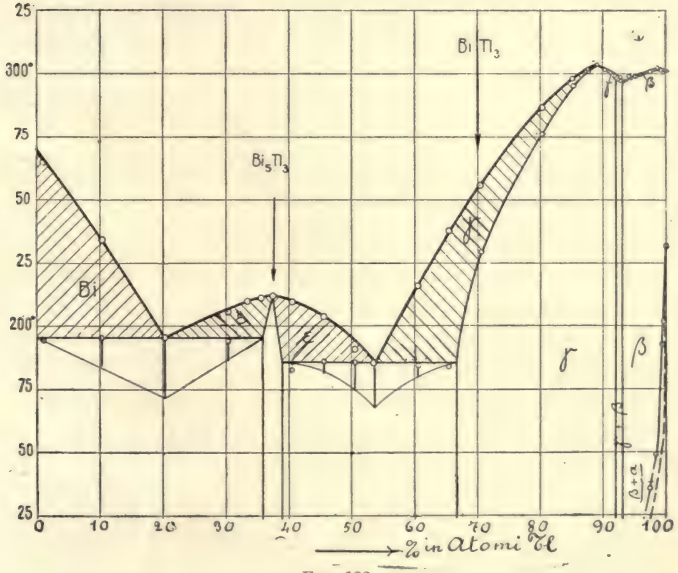

FIG. 122.

cease to exist. The second maximum is at 12·05 per cent. of bismuth and 303·7°; between 5·9 and 33 per cent. of bismuth more solid solutions are formed. The third maximum is at 62·8 per cent. and 211·7°, and a further series of solid solutions ϵ crystallises from 55 to 64 per cent. of bismuth. The last branch of the curve corresponds to the separation of pure bismuth without any notable formation of solid solutions.

[1] *Zeit. anorg. Chem.*, **83**, 200 (1913).

According to Kurnakoff and his co-workers, the three maxima do not correspond to any rational atomic proportions. Chikashigé, though admitting the irrationality of two of the maxima, maintains that the third corresponds to the formula Bi_5Tl_3.

Kurnakoff and his collaborators from a study of the electrical conductivity, compressibility, hardness and microscopic structure of these alloys conclude that no definite formula can be assigned to correspond with any of the three maxima.

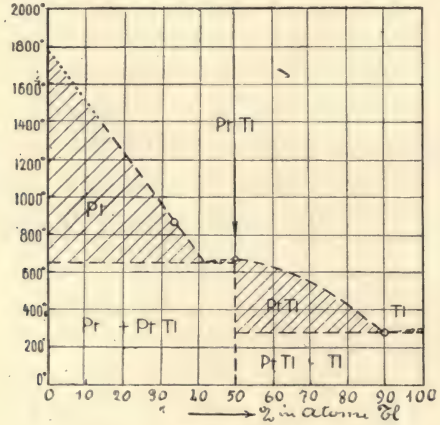

FIG. 123.

Thallium-iron.—Nothing is known of the alloys of these metals. Isaac and Tammann,[1] who made some preliminary investigations, obtained no results, the boiling point of thallium being lower than the melting point of iron. They did in fact observe a certain lowering of the melting point of iron by thallium, but the thallium very quickly distilled off unaltered.

Thallium-platinum.—According to Hackspill,[2] thallium

[1] *Zeit. anorg. Chem.*, **55**, 61 (1907).
[2] *C. R.*, **146**, 820 (1908).

and platinum form a compound TlPt. Thallium dissolves easily in platinum. The curve (Fig. 123) shows that the addition of platinum to thallium causes lowering of the melting point by a few degrees. With increase of the content in platinum there occurs, at 50 per cent. and 685°, the separation of crystals of the formula PtTl. The curve then falls slightly and subsequently rises so that at 70 per cent. of platinum it reaches about 1000°. Platinum forms solid solutions with thallium. Between the compound and platinum no solid solutions are formed according to Hackspill's observations.

Compounds of Metals of Group IV. with Metals of other Groups.

Compounds of Tin.

Antimony-tin. — It is probable, though not certain, that these metals combine to form a compound SbSn. The system has been studied by Reinders,[1] Gallacher[2] and Williams.[3] The diagram constructed by the last named is shown in Fig. 124. On cooling melts rich in antimony, a series of mixed crystals of the two metals separates. At 420°, from 50 to 90 per cent. of antimony there forms, after separation of mixed crystals, a new crystalline species surrounding the mixed crystals rich in antimony. There are no corresponding arrests on the cooling curve but only slackening. At 243°, however, up to 50 per cent. of antimony, distinct arrests are noted. The mixed crystals in all probability are transformed into SnSb crystals at 50 per cent. by addition of tin. The existence of this compound is, however, not well established.

Tin-bismuth. — Chemical combination between these metals, although stated to take place by Tammann,[4] is

[1] *Zeit. anorg. Chem.*, **25**, 113 (1900).
[2] *J. Phys. Chem.*, **10**, 93 (1906).
[3] *Zeit. anorg. Chem.*, **55**, 14 (1907).
[4] *Lehrb. d. Metall.*, p. 222 (1914), Leipzig.

excluded by the complete investigations of Mazzotto.[1] This is also shown by the experimental work recorded on p. 45.

The system has also been studied by Stoffel [2] and Lepkovsky.[3]

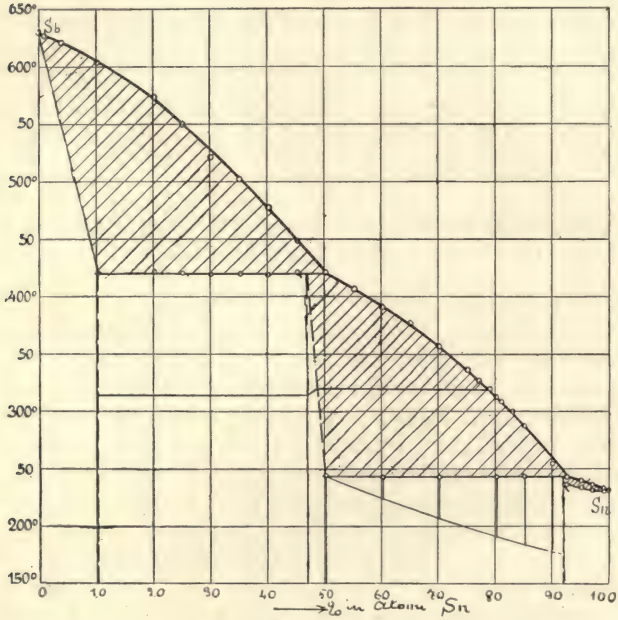

FIG. 124.

Tin-manganese.—Manganese forms with tin the compound $SnMn_4$, $SnMn_2$ and possibly SnMn. The diagram (Fig. 125) has been traced by Williams.[4] The three compounds are represented by three breaks in the curve, the first at 988° and 80·1 per cent. of magnanese, the second at

[1] *Mem. Inst. Lomb.*, **16**, (1886), and *Nuovo Cimento*, **18** (1900).
[2] *Zeit. anorg. Chem.*, **53**, 148 (1907).
[3] *Ibid.*, **59**, 287 (1908).
[4] *Ibid.*, **55**, 26 (1907).

898° and 64·8 per cent. of manganese, and the third at 541° and 15 per cent. of manganese. The reaction which gives rise to the latter does not, however, take place to completion, but part of the crystals of $SnMn_2$ surrounded by SnMn are deposited in the presence of the melt.

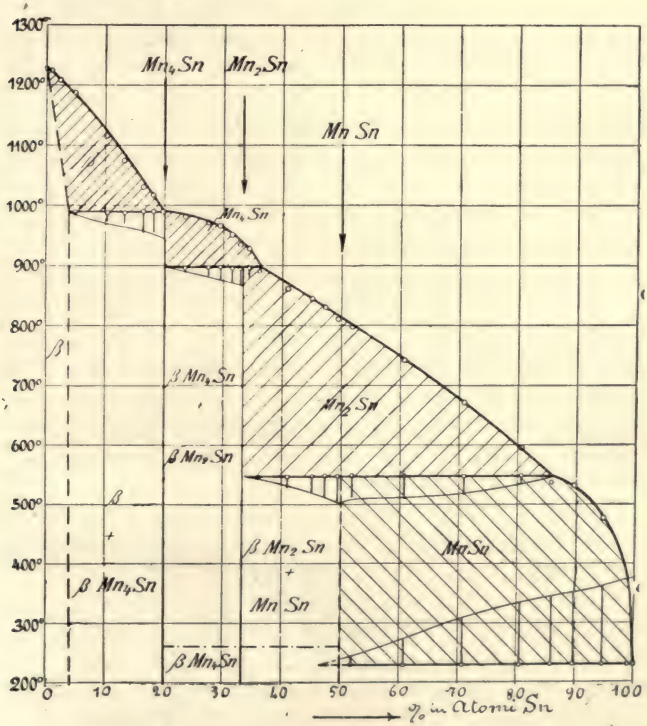

FIG. 125.

There is a series of mixed crystals rich in manganese, the last number of which is the saturated mixed crystal with about 4 per cent. of tin. $SnMn_4$ is less brittle than manganese and, when polished, has a surface like that of steel. Hardness, 4·5. $SnMn_2$ is similar in colour to the preceding

compound and its hardness is 3—4. SnMn has a silvery white colour. These compounds are weakly attacked by acids. $SnMn_4$ is magnetic, $SnMn_2$ to a less degree, and SnMn least of the three.

Tin-iron.—There is doubt as to the occurrence of compounds of tin and iron. Levin and Tammann [1] and Isaac and Tammann [2] have studied the system and constructed a diagram (Fig. 126). Iron and tin do not mix in all proportions in the liquid state. At 1140°, between 32 and 79 per cent. of tin, two strata are found, one rich in iron and the other rich in tin. The greatest arrest due to crystallisation occurs at 32 per cent. of tin. At 893° between 10 to 93 per cent. tin, arrest points occur. The mixed crystal γ reacts with the melt containing 79 per cent. of tin to form a compound. The thermal effect is, however, small and shows no marked maximum. From 10 to 95 per cent. tin there occur at 780° further arrests which may be due to polymorphic transformation in the compound formed at 893.°

There is a distinct maximal arrest at 24 per cent. of tin which should correspond to a compound $SnFe_3$. At 496°, between 35 and 97·5 per cent. of tin, arrests occur which, however, have not been explained.

These alloys display notable magnetic properties ; the tin content has a marked influence on the temperature at which iron loses its magnetic permeability.

Tin-cobalt.—Two compounds are formed between these metals, namely, SnCo and $SnCo_2$. The system has been studied by Levkonja [3] and Zemczuzny and Belynski.[4] The results obtained by these workers are in accordance. Levkonja's diagram is shown in Fig. 127. The curve shows a maximum and a break, the maximum at 1150° and 33 per cent. of tin, corresponding to $SnCo_2$, and the break at 948° and 75 per cent. of tin, corresponding to the compound

[1] *Zeit. anorg. Chem.*, **47**, 141 (1905).
[2] *Ibid.*, **53**, 281 (1907).
[3] *Ibid.*, **59**, 298 (1908).
[4] *Ibid.*, p. 368.

CoSn,[1] which undergoes a polymorphic transformation at 520°. At 229° there are arrest points which are due to the eutectic between CoSn and pure tin.

The compounds CoSn and Co_2Sn are harder than their

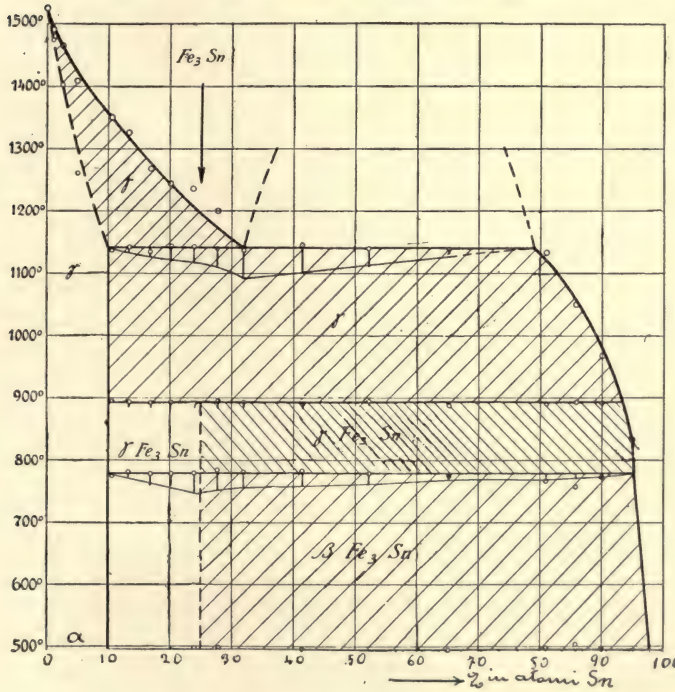

FIG. 126.

component elements. With regard to magnetic properties the cobalt-tin alloys may be divided into two groups ; up to 50 per cent. of cobalt, magnetic properties are wanting ; the alloys containing more than 50 per cent. of cobalt are increasingly magnetic with increase of cobalt.

[1] The composition of this compound is indicated by the position of the maximal arrests at 948° and 520°.—*Translator's Note.*

Tin-nickel.—Nickel combines with tin, and the following compounds have been shown to exist by thermal analysis :

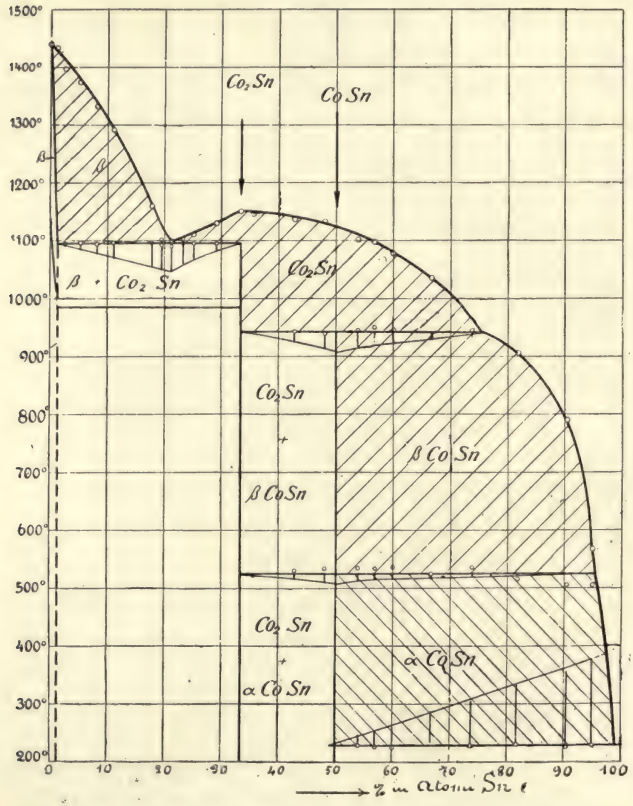

FIG. 127.

Ni_3Sn_2, Ni_3Sn, and Ni_4Sn. The diagram (Fig. 128) was traced by Voss.[1] At the beginning of the curve mixed crystals separate. At 1135° and 82·5 per cent., eutectic

[1] *Zeit. anorg. Chem.*, **57**, 38 (1908).

crystallisation occurs. At 1162° and 60 per cent. of nickel, the compound Ni_3Sn_2 is formed. From 64 to 42 per cent. of nickel a lack of miscibility is noted and two liquid phases

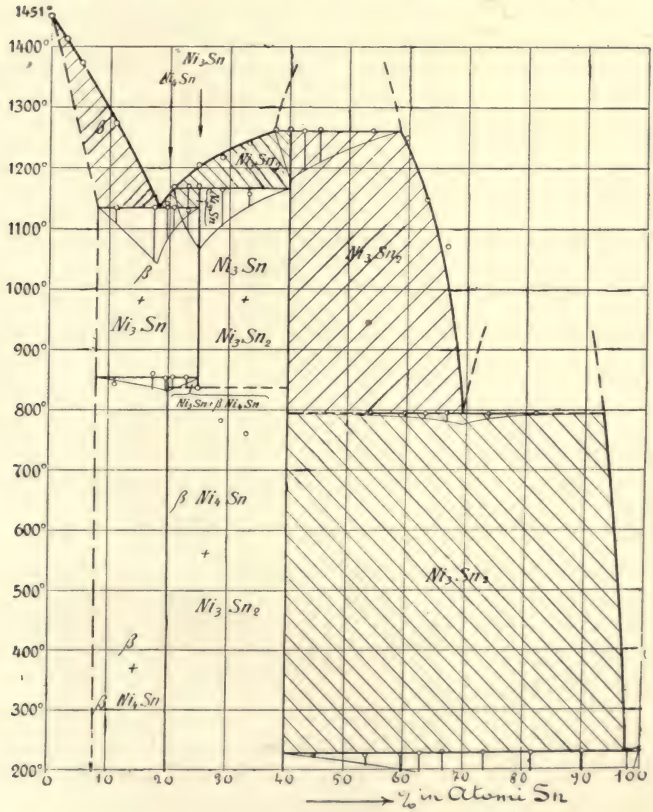

FIG. 128.

occur. Another gap in miscibility occurs also between 30 and 7 per cent. of nickel; these melts are in equilibrium with the compound Ni_3Sn_2. At 885°, arrests are noted between 85 and 60 per cent. of nickel with a maximum for

67 per cent. (by weight) of nickel, corresponding probably to the compound Ni_4Sn. Microscopic analysis confirms the thermal data.

Tin-platinum.—Platinum forms the following compounds with tin: $SnPt_3$, SnPt, Sn_3Pt_2, and Sn_8Pt_3. The system was studied by Doerinckel [1] and is given in Fig. 129. $SnPt_3$

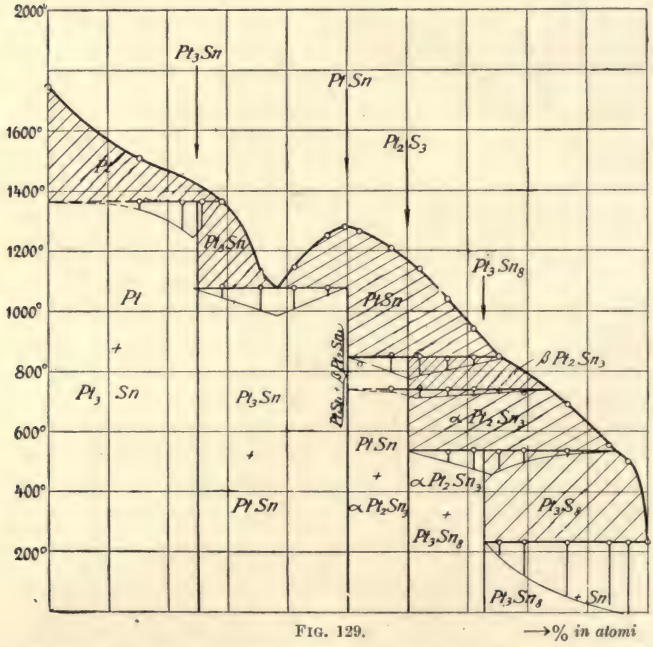

FIG. 129.

is formed at about 1375° and 75 per cent. of platinum by reaction between crystals of platinum and the melt containing 70 per cent. of platinum. Crystals of SnPt then begin to separate; the maximum occurs at 50 per cent. and 1281°. At 846° crystals of SnPt react with the melt of composition β.

[1] *Zeit. anorg. Chem.*, **54**, 35 (1907).

The arrests at this temperature show a maximum for about 40 per cent. platinum. According to Doerinckel this maximal arrest is due to the compound Sn_3Pt_2. A small difference between the position of the observed maximal arrest and that required for the compound may be explained by the formation of a layer around the crystals which hinders the completion of the reaction, as appears evident on microscopical examination. A further series of arrests occur at 738° with a maximum at 40 per cent. platinum; these indicate, therefore, a polymorphic transformation of the compound Sn_3Pt_2. At 537° this modification of the compound Sn_3Pt_2 reacts with the melt having 5 per cent. of platinum, giving a compound at 28 per cent. of platinum which is probably Pt_3Sn_8.

The hardness of these alloys grows with increase of platinum content; at 40 per cent. it is equal to that of calc spar, at 60 per cent. to that of fluor spar. Maximum hardness is found at 80 per cent., at which it is slightly greater than that of apatite. Mineral acids attack these alloys in inverse proportion to their platinum content.

Cerium Compounds.

Cerium-bismuth. — These alloys have been studied by Vogel,[1] who noted the formation of the compounds $BiCe_3$, Bi_3Ce_4, BiCe, and Bi_2Ce. The maximum (see Fig. 130), which is found at the high temperature of 1630°, corresponds to the compound Bi_3Ce_4, which requires a concentration of about 53 per cent. (by weight) of bismuth. At 1400°, as shown by microscopical analysis, Bi_3Ce_4 reacts with the melt forming the compound $BiCe_3$ which has an obscured maximum at 32 per cent. of bismuth. This compound has its primary separation along *B C* and at 757° crystallises eutectically with cerium. Small thermal effects are noted between 830° and 860°, due to reactions between bismuth and small quantities of lanthanum and didymium present as

[1] *Zeit. anorg. Chem.*, **84**, 327 (1914).

impurities in the cerium used in the experiment. At 1525° and about 60 per cent. of bismuth, the compound BiCe is formed which separates primarily between 61 and 82 per cent. of bismuth. At 882° it reacts with the melt forming a

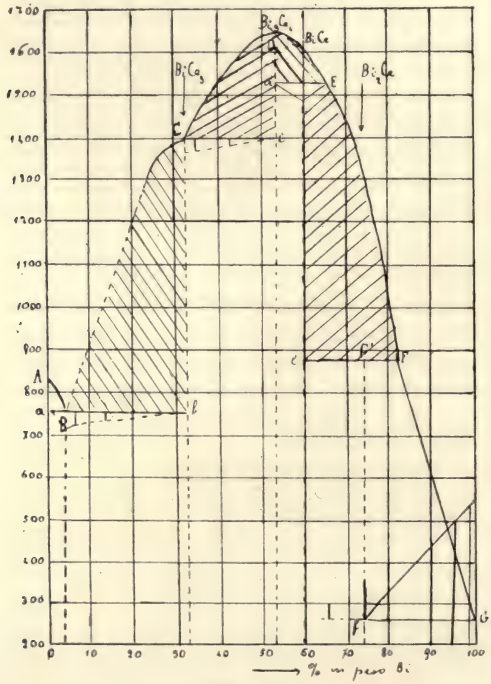

FIG. 130.

compound richer in bismuth (Bi_2Ce, requiring 74·8 per cent. bismuth).

These alloys are very easily oxidisable ; exposed to air, they are quickly altered to a black powder and are energetically attacked by acids. The hardness is greatest for medium concentrations.

Cerium-iron.—These alloys, which are noteworthy for their pyrophoric properties, are known through the work of Auer von Welsbach.[1 and 2]

Compounds of Lead.

Lead-bismuth.—It is doubtful whether chemical combination occurs between lead and bismuth. The system has been studied by Mazzotto,[3] Kapp,[4] Stoffel,[5] and Barlow.[6] The two branches of which the equilibrium curve consists intersect at 125° and 55 per cent. of bismuth. According to Kapp, the thermal effects corresponding to eutectic crystallisation occur from 36 to 98 per cent. of bismuth, which would show that up to 36 per cent. of bismuth solid solutions are formed.

Lead-palladium.—Palladium forms a number of compounds with lead, namely, Pb_2Pd, PbPd, Pb_3Pd_4, $PbPd_2$ and $PbPd_3$. Some doubt exists as to the occurrence of the last; the first compound has been admitted to exist by Pushin and Paschsky,[7] as a result of their measurements of the electrolytic potential of these alloys. The system has been studied by Ruer,[8] whose diagram is reproduced in Fig. 131. Pb_2Pd separates at 454° and 30·49 per cent. of palladium. This compound melts without decomposition. From 40 to 75 per cent. of palladium, three series of arrests indicate three

[1] *D. R. P.*, 154,807 (1903).

[2] Vogel has recently published a paper on the alloys of cerium and iron (*Zeit. anorg. Chem.*, **99**, 25 (1917)). He found that the metals are miscible in all proportions and form two compounds, namely, $CeFe_2$ and Ce_2Fe_3. The first is changed into the second at 773°; Ce_2Fe_3 decomposes at 1085° into a liquid and a solid solution rich in iron; the solution contains 15 per cent. of cerium and becomes poorer in this element on cooling. The compound $CeFe_2$ is magnetic, but loses its magnetic properties at 116°. It is not certain whether the second compound is magnetic. Pyrophoric properties are exhibited by these alloys, those with 70 per cent. of cerium displaying this property to a most marked degree so that a slight scratch is sufficient to cause ignition. The compounds are hard and brittle; they are not oxidised at ordinary temperatures.—*Translator's Note.*

[3] *Memt. Ist. Lomb.*, (3), 7 (1886), and *Nuovo Cimento*, **18** (1909).

[4] *Drud. Ann.*, **6**, 754 (1901).

[5] *Zeit. anorg. Chem.*, **53**, 150 (1907).

[6] *J. Am. C. S.*, **32**, 1394 (1910); *Zeit. anorg. Chem.*, **70**, 183 (1911).

[7] *Zeit. anorg. Chem.*, **62**, 360 (1909).

[8] *Ibid.*, **52**, 347 (1907).

compounds, each of which on melting decomposes into a melt, and a new species of crystal. The first is formed at 500° and 50 per cent. of palladium and is the compound PbPd. The second compound is indicated by a weak maximal arrest at 595° and 56 per cent. of palladium ; the most probable formula is Pb_3Pd_4. The formulæ Pb_6Pd_7, Pb_5Pd_6, and Pb_4Pd_5 are less probable. The third compound

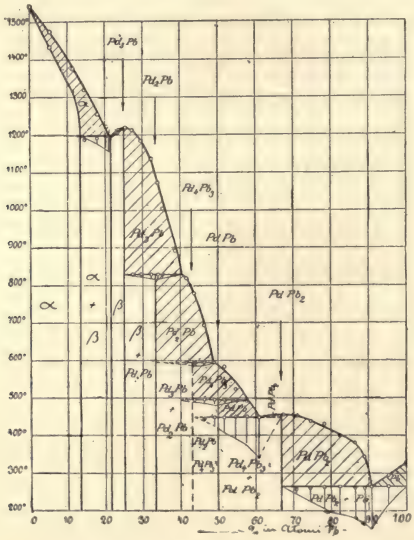

FIG. 131.

gives a maximal arrest for 67 per cent. of palladium at 830° ; here again the maximum is not well defined. The formula of the last compound should be $PbPd_2$. The fifth and last compound, $PbPd_3$, gives a maximum on the fusion curve at 1230° and 75 per cent. of palladium.

The hardness of these alloys is greater than that of lead, and increases up to about 78 per cent. of palladium, where it reaches a maximum (5), and afterwards decreases. Alloys

with 27 to 74 per cent. of palladium are very brittle; the remainder are not so markedly brittle.

Lead-platinum.—These metals combine to form a compound PbPt. The existence of two other compounds is doubtful. The system, of which the diagram is reproduced in Fig. 132, was studied by Doerinckel. At 40 per cent. of

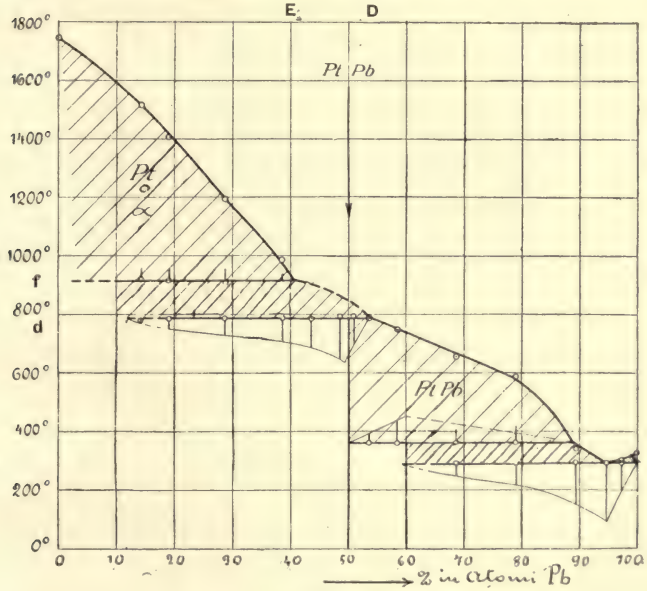

FIG. 132.

lead, crystals of platinum react with the melt of composition *E* forming a compound which has not been well defined by thermal analysis. The irregularity of the thermal arrests lead to the supposition that the reaction does not proceed to completion on account of the crystals becoming coated with a sort of protecting covering, but microscopical examination has not rendered this certain. Between *D* and *E*, a gap occurs. At the composition represented by *D*, a further

reaction occurs at a temperature of 787°. The arrests show a maximum at 49·5 per cent. of lead which gives the formula of the resultant compound as PbPt. At 350° and at composition *C*, a further reaction occurs whereby another compound may be formed, but its composition cannot be well determined on account of the reaction being incomplete as in the case of the first compound. Doerinckel[1] states that it certainly contains less than 40 per cent. of platinum.

These alloys are harder than their components ; at 30 per cent. of platinum the hardness is almost equal to that of calc spar ; at 45 per cent. it is almost equal to that of fluor spar and increases up to 85 per cent. The alloys are easily oxidised and are attacked by nitric acid, those with less than 50 per cent. of platinum being most easily attacked.

Pushin and Laschtschenko [2] have studied these alloys by making measurements of electrolytic potential and demonstrated the existence of two compounds, PbPt and Pb_2Pt.

Compounds of Metals of Group V. with Metals of the other Groups.

Compounds of Antimony.

Antimony-manganese.—These metals combine, giving rise to two compounds, Sb_2Mn_3 and $SbMn_2$. The system was studied by Williams,[3] and its diagram is given in Fig. 133. It shows a very much flattened maximum and a discontinuity in the fusion curve. The maximum is at 66·9 per cent. of manganese and 919° and corresponds to the compound $SbMn_2$. The discontinuity which occurs at 852° indicates the compound Sb_2Mn_3 (60·3 per cent. Mn). The compounds form two series of mixed crystals, $SbMn_2$ from 65 to 69 per cent. of manganese and Sb_2Mn_3 from 50 to 60 per cent. of manganese. They have a silvery-grey colour and

[1] *Zeit. anorg. Chem.*, **54**, 361 (1907).
[2] *Ibid.*, **62**, 34 (1909).
[3] *Ibid.*, **55**, 3 (1907).

resemble each other closely. On treating with 10 per cent. $FeCl_3$, Mn_2Sb_3 is more powerfully attacked than the other compound and assumes a deeper yellow colour.

The two compounds are less hard than their components ; the hardness of the first is 3 to 4 and that of the second 2 to 3. The antimony-manganese alloys exhibit magnetic properties which, however, decrease with rise of manganese content. Sb_2Mn_3 is less magnetic than $SbMn_2$.

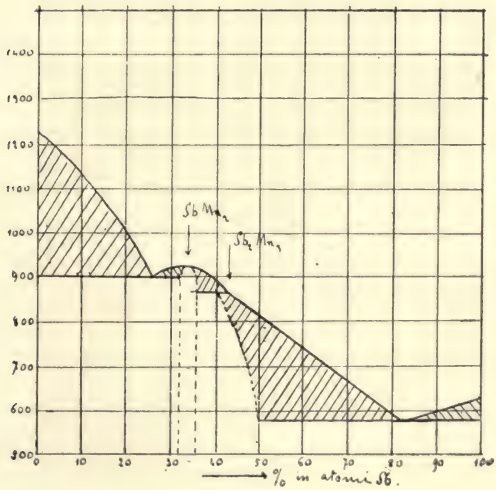

FIG. 133.

Antimony-iron.—Two compounds are formed, namely, Sb_2Fe and Sb_2Fe_3. The system has been studied by Kurnakoff and Konstantinoff.[1] In the diagram (Fig. 134) the curve shows a discontinuity at about 732°, at which temperature arrests occur on the cooling curve. The compound indicated by these arrests is $FeSb_2$ (66·6 per cent. of antimony). The other compound is indicated by a maximum at 1014° and 41·17 per cent. of iron. It melts without decom-

[1] *Zeit. anorg. Chem.*, **58**, 1 (1908).

position. At the point C the equilibrium $3FeSb_2 \rightleftarrows Fe_3Sb_2 + 4Sb$ occurs. If the temperature falls below 732°, the compound Fe_3Sb_2 forms, but considerable time is required for the completion of the reaction. Solid solutions are indicated from 41 to 46 per cent. antimony and from 95 to 100 per cent. antimony.

These compounds tend to occur in the labile state.

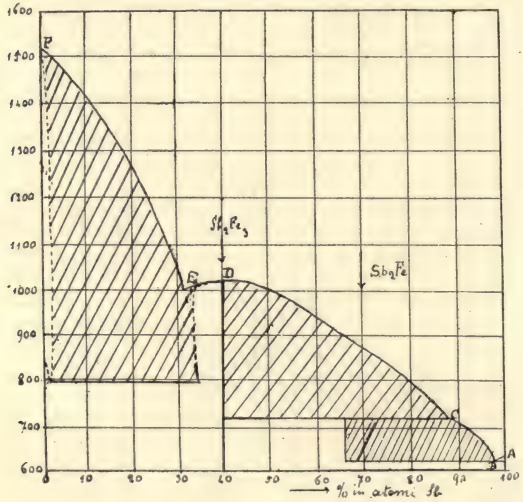

FIG. 134.

Antimony-cobalt.—Two compounds are formed between these metals, namely, CoSb and $CoSb_2$. The system has been studied by Kurnakoff and Podkapajeff,[1] and by Levkonja.[2] The results obtained by these workers are generally concordant. The diagram (Fig. 135) is due to Levkonja. It shows a maximum at 1191° and 50 per cent. of antimony, corresponding to the compound CoSb. Between

[1] *Journal Russ. phys.-chem. Soc.*, **38**, 463 (1906).
[2] *Zeit. anorg. Chem.*, **59**, 305 (1908).

50 and 84 per cent. of antimony this compound reacts with the melt *d* forming the compound $CoSb_2$. Arrest points at 616° indicate the formation of an eutectic alloy. The alloys up to 67 per cent. of antimony show magnetic properties, which increase in intensity with increase in cobalt; the alloy with 90 per cent. of cobalt is most magnetic. The two compounds are, however, non-magnetic.

Antimony-nickel.—The following compounds are formed :

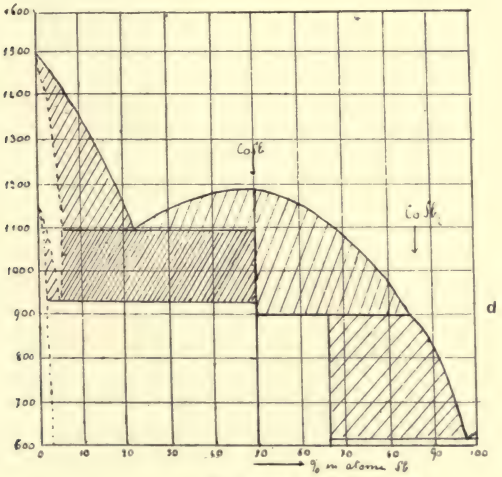

FIG. 135.

Sb_5Ni_4, SbNi, Sb_2Ni_5, and $SbNi_4$. The system has been studied by K. Losseff.[1] The curve (Fig. 136) shows two distinct maxima. The first corresponds to the compound NiSb and occurs at 1158° and 50 per cent. of nickel; the second at 1170° and 72 per cent. of nickel indicates the compound Ni_5Sb_2. Beginning at 4 per cent. of nickel, two arrests are observed; microscopical analysis of these alloys show that at 50 per cent. and 612°, the compound NiSb reacts with

[1] *Zeit. anorg. Chem.*, **49**, 63 (1906).

the melt giving a compound whose formula is probably Ni_4Sb_5. The compound NiSb by addition of nickel forms a series of mixed crystals, of which the saturated mixed crystal is at 1072° and 56 per cent. of nickel. At 677° in alloys from 97 to 73 per cent. of nickel, a reaction occurs which gives a series of arrests having their maximum at 80 per cent. Microscopical examination reveals that at this temperature a new species of crystal is formed surrounding the

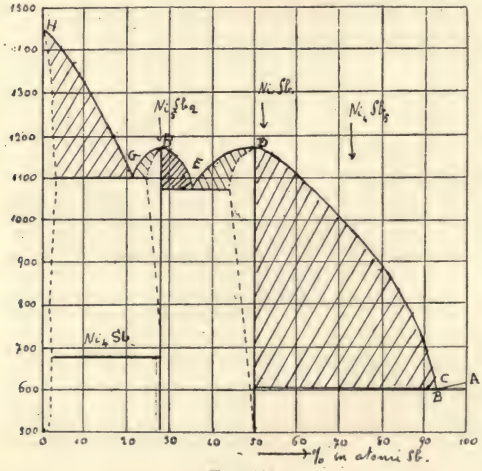

FIG. 136.

saturated mixed crystals and separating them from the eutectic. The formula Ni_4Sb corresponds to this compound. Above 677° it decomposes into two saturated mixed crystals containing 97 and 73 per cent. of nickel respectively.

The compound NiSb has a red colour and is very hard and brittle. It dissolves in nitric acid, but is not attacked by hydrochloric and sulphuric acids or by strong bases. Ni_5Sb_2 is harder than NiSb, but not so brittle; it is finely granular and has the colour of fused iron.

Antimony-palladium.—These metals combine to form the

compounds Sb_2Pd, SbPd, Sb_3Pd_5, and $SbPd_3$. The system, whose diagram is shown in Fig. 137, was investigated by W. Sander.[1] The first compound separates at 30·7 per cent. (by weight) of palladium and about 670°, the second at 47 per cent. of palladium and 805°, the third at about 62 per cent. and 840°, and the fourth at 72·5 per cent. and 1220°. The

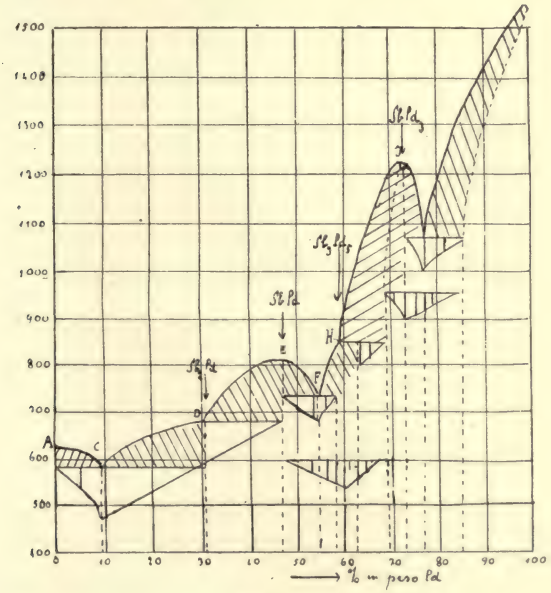

FIG. 137.

compound Sb_3Pd_5 forms mixed crystals, on the one hand with palladium as far as 61·5 per cent., and on the other hand with antimony as far as 57·5 per cent. of palladium. At 733° the saturated mixed crystal forms the eutectic *F* with PdSb. From 47 to 68·5 per cent. of palladium, arrests are noted from 525 to 532° with a maximum at 60 per cent., the arrests from 57·5 to 50 per cent. of palladium being at a

[1] *Zeit. anorg. Chem.*, **75**, 97 (1912).

somewhat higher temperature than those between 60 and 55 per cent. These thermal effects are accompanied by a change in structure of the alloys concerned. The mixed crystal corresponding to Pd_5Sb_3 passes from an α to a β form without change of composition. The mixed crystals, richer in palladium, break up at a temperature which diminishes with increase of palladium into α Pd_5Sb_3 and a saturated mixed crystal. The formation of the compounds of

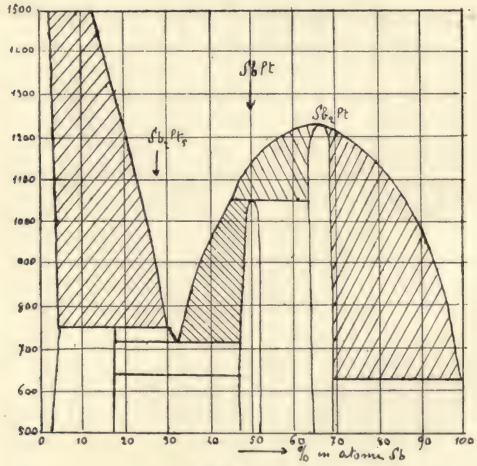

FIG. 138.

palladium and antimony is accompanied by marked supercooling.

Alloys up to 72 per cent. of palladium are very brittle, particularly the mixed crystals of the compound Pd_3Sb between 72·5 and 68·5 per cent. of palladium.

Antimony-platinum.—These metals form the compounds Sb_2Pt and Sb_2Pt_5. The existence of a compound SbPt is doubtful. The system was studied by Friedrich and Leroux.[1] The diagram is given in Fig. 138. A maximum

[1] *Métall.*, **6**, 1 (1905).

due to Sb_2Pt occurs at 1230° and 66·6 per cent. of antimony. Another compound is shown on the curve nearer the antimony axis which crystallises peritectically. Friedrich places the peritectic point at 50 per cent. of antimony (SbPt).

At 710° and at 752° and about 16 per cent. of antimony, thermal effects are observed probably due to the peritectic formation of other crystals round the crystals of platinum. Finally at about 28 per cent. of antimony, the compound Sb_2Pt_5 is formed. Friedrich and Leroux have not discovered whether solid solutions are formed or not.

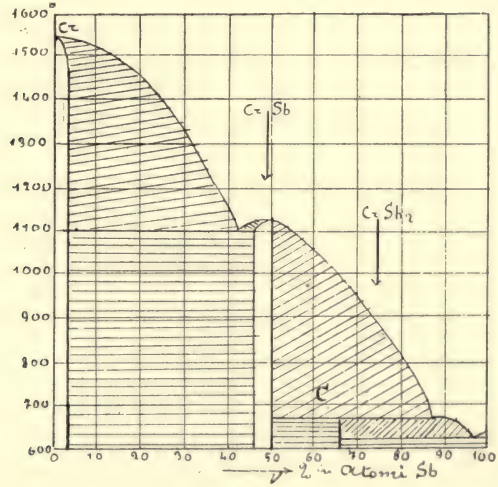

FIG. 139.

Platinum dissolves antimony to a slight extent ; the actual limit of saturation is unknown because alloys with less than 10 per cent. of antimony have not been examined. Antimony crystallises practically pure at the eutectic point lying near its own axis.

Antimony-chromium.—Antimony and chromium form two compounds, Sb_2Cr and SbCr, as noted by Williams.[1] In the

[1] *Zeit. anorg. Chem.*, **55**, 8 (1907).

diagram (Fig. 139) a maximum occurs at 50·1 per cent. of chromium and about 1110°, corresponding to the compound SbCr. At 675°, crystals of SbCr, formed by primary separation, react with the melt forming at 32·96 per cent. of chromium, the compound Sb_2Cr. Both compounds form mixed crystals with the pure components.

SbCr is very brittle; freshly broken it has a dark grey

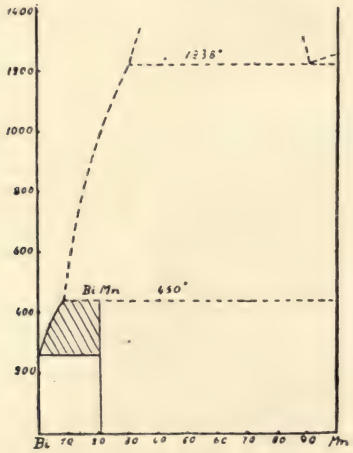

FIG. 140.

colour; it is easily attacked by dilute acids, assuming a black colour. Its hardness is 3 to 4. Sb_2Cr has a silvery white colour and is as brittle as SbCr. It is slightly attacked by dilute acids, which turn it yellow. Hardness 2 to 3.

COMPOUNDS OF BISMUTH.

Bismuth-manganese.—Wedekind and Weit [1] have studied the capacity for combination of these metals and have obtained crystals of formula MnBi. A study has also been

[1] *Ber.*, **44**, 2063 (1911).

made by Hilpert and Dieckmann.[1] The fusion diagram has been investigated by Bekier [2] and by Parravano and Perret.[3] The chief characteristics of the diagram as described by these authors are in fair agreement. The diagram is given in Fig. 140. The two metals are partially miscible in the liquid state and form a compound BiMn which, according to Parra-

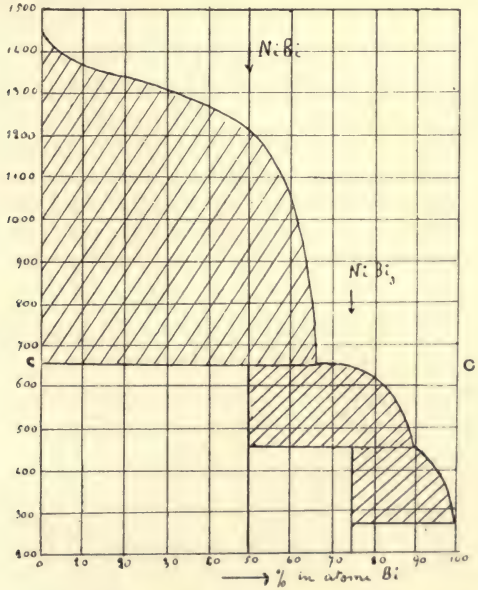

FIG. 141.

vano and Perret, is formed peritectically at 400°. The curve is fairly simple; a gap in miscibility extends over the greater part of the diagram (from 30 to 93 per cent. of manganese). As the results are not at present clearly explained, it is unnecessary here to enter more minutely into a description of this system.

[1] *Ber.*, **44**, 2831 (1911).
[2] *Int. Z. f. Metall.*, **7**, 83 (1914).
[3] *Gazz. Chim. Ital.*, **45**, I., 390 (1915).

Bismuth-nickel.—Two compounds are formed, namely, Bi_3Ni and BiNi. The system has been investigated by Portevin [1] and Voss.[2] Fig. 141 shows the diagram of the system. The first compound separates at 437° and about 25 per cent. of nickel, the second at 638° and about 50 per cent. of nickel. The separation of the compound BiNi from the melt and the reaction of the melt *C* with the mixed crystals rich in nickel take place with super-cooling, and the temperature of the reaction on the horizontal *C c* is consequently somewhat lower in practice than it should be. Voss, however, has some doubt as to the exactitude of the formula BiNi.

Bismuth is only slightly soluble in nickel—not more than ·5 per cent., while the solubility of nickel in bismuth is less than ·5 per cent. The eutectic is very near the melting point of bismuth at about 270°.

Compounds of the Metals of Group VI. with Metals of the other Groups.

Chromium-iron.—Iron forms a compound with chromium whose composition has not yet been well ascertained. The system has been studied by Treitschke and Tammann.[3]

The fusion curve has an abnormal form. The magnitude of the thermal effects due to primary crystallisation diminishes slowly from iron to chromium. The temperature at which the second arrest occurs sinks with increase of iron content up to 40 per cent. of iron and then rises up to the melting point of pure iron. The temperature of the third slackening in the cooling curves, which is at 1260° for melts with 50, 40 and 30 per cent. of chromium, is fairly constant and corresponds to an eutectic crystallisation. As in the case of iron-molybdenum, Treitschke and Tammann attribute the abnormalities to the slow velocity of formation of

[1] *C. R.*, **145**, 1168 (1907).
[2] *Zeit. anorg. Chem.*, **57**, 52 (1908).
[3] *Ibid.*, **55**, 403 (1907).

the compound. While there is only a limited range of mixed crystals in the system iron-molybd num, chromium and iron form a continuous series with the compound which occurs.

Chromium-cobalt.—Chromium combines with cobalt, but the formula of the compound is not known with certainty. The system has been studied by Levkonja.[1] In the diagram (Fig. 142) there are noted at 1225° from 45 to 85 per cent. of chromium, distinct arrests ; they are, however, so small that it has not been possible to distinguish a maximal arrest.

Chromium-nickel.—As in the preceding systems, it has not

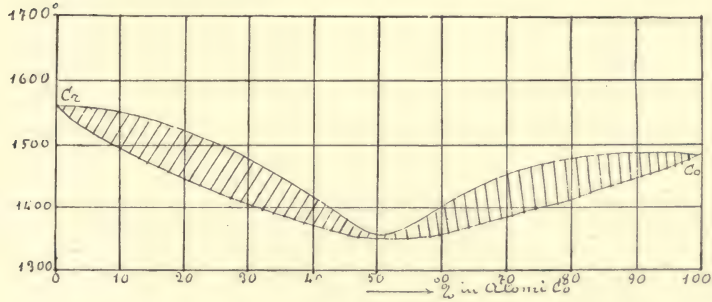

FIG. 142.

been possible hitherto to ascertain the nature of the chemical combination between chromium and nickel. The system was studied thermally and micrographically by Voss.[2]

The diagram is given in Fig. 143. The two metals mix in all proportions in the liquid state, apart from a gap in miscibility between 42 and 45 per cent. of nickel. The curve is similar to that for chromium-cobalt and shows a minimum below 1300° and at 42 per cent. of nickel. The corresponding alloy, examined microscopically, shows an eutectic structure.

Alloys with a high nickel content are hard even at high temperatures (500°), and are very resistant to chemical reagents. In nickel containing 2 per cent. of chromium the

[1] *Zeit. anorg. Chem.*, **59**, 325 (1908).
[2] *Ibid.*, **57**, 34 (1908).

temperature of magnetic transformation is lowered by 100° ; with 10 per cent. of chromium, nickel is non-magnetisable even at ordinary temperatures.

Compounds of Molybdenum.

Molybdenum-iron.—The system molybdenum-iron has been studied up to 60 per cent. of molybdenum by Lautsch and Tammann.[1] In this range, the metals form a compound whose formula has not yet been correctly ascertained. The fusion diagram shows irregularities. It has not the appear-

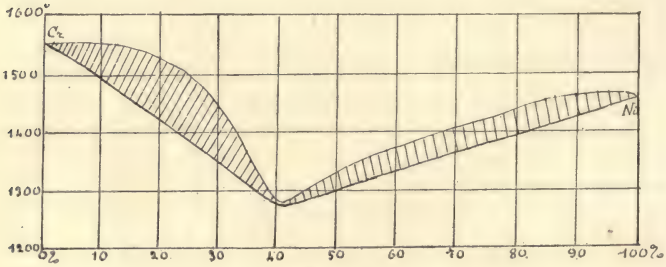

Fig. 143.

ance of a normal binary system, but presents certain characteristics of ternary systems. As in the case of chromium-iron, it is held that a compound is formed whose velocity of formation and decomposition is small compared to the velocity of the changes produced in the melt by crystallisation. In their study the authors distinguish between the ultimate composition of the melt referred to its components and the proximate composition determined by the concentrations of the elements and the unknown compound formed.

Molybdenum-cobalt.—Molybdenum forms with cobalt the compound MoCo. The system has been studied by Raydt and Tammann.[2] The diagram (Fig. 144) shows that at first

[1] *Zeit. anorg. Chem.*, **55**, 388 (1907).
[2] *Ibid.*, **83**, 246 (1913).

mixed crystals separate along the curve $A\,F$. The saturated mixed crystal F contains 28 per cent. (by weight) of molybdenum. At 1485° and 62 per cent. of molybdenum, the compound MoCo is formed. Below $D\,B$ there separates either molybdenum or mixed crystals poor in cobalt. It is improbable that another compound richer in molybdenum is formed because the arrests at 485° only disappear near the

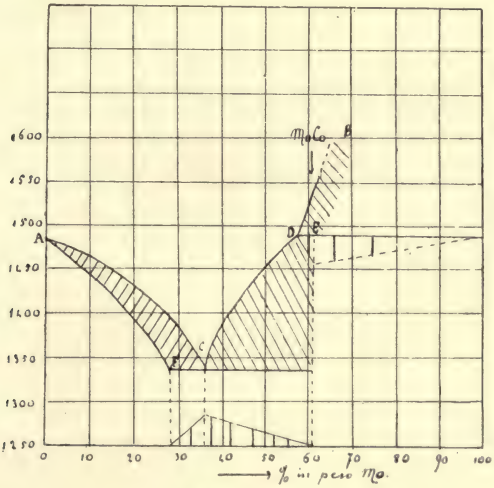

FIG. 144.

molybdenum axis. The compound crystallises in long needles.

Molybdenum-nickel.—The compound MoNi is formed between these metals as reported by Baar,[1] who has described cooling curves from 1600° to 700°. From 0 to 33 per cent. of molybdenum, mixed crystals separate ; from 33 to 49·5 per cent., an eutectic separates, after the primary separation, composed of the saturated mixed crystal with 33 per cent. of

[1] *Zeit. anorg. Chem.*, **70**, 352 (1911).

molybdenum and a compound which solidifies in dendritic crystals at 1340° from 49·5 to 54 per cent. of molybdenum.

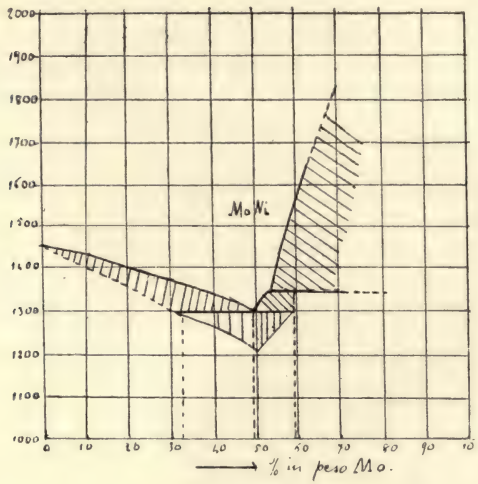

FIG. 145.

The formula attributed to it is MoNi. From melts containing 54 to 100 per cent. of molybdenum, there crystallise in all probability mixed crystals poor in nickel.

CHAPTER VI.

Heteropolar Intermetallic Compounds.

General Remarks.

In this class we may include certain compounds which boron, carbon, silicon, phosphorus, arsenic, sulphur, selenium and tellurium form with metals. Such compounds are metallic in character, and in many respects must therefore be studied together with the great category of chemical compounds between metals. Each of these classes of compounds has its own character, but general similarities in their properties necessitate their being grouped together. These compounds have usually a simple composition which, in the majority of cases, is related to the known saline valencies of their components; this regularity is rather apparent than real, because important exceptions occur among these heteropolar combinations, as will be seen in the following pages.

Of the carbides, only those have been mentioned which show metallic properties, to however slight a degree. The thermal method has been applied in only a few cases, but where it has been possible to use this method of investigation the results have been striking, as in the case of the studies on steels.

Those of the carbides which do not act upon water are of great importance in metallurgy, while those which can decompose water are of some theoretical interest. According to Moissan [1] the carbides are of geo-genetic importance. Many elements combine easily with carbon, and a general regularity

[1] Moissan carried out the first notable researches on the carbides, using the electric furnace. *Cf. Le four électrique.* See also *Les carbures métalliques*, Paris, 1904; Ahrens, *Die Metallcarbide—Chem.-techn. Vorträge*, I. (1896), and O. Hönigschmid, *Karbide u. Silizide*, Halle, 1914.

has been observed which is worth mention. *The elements of the even series of the periodic system react easily with carbon; the elements of the odd series either do not react or else, if they do, show a close analogy with the other metals of the even series.* Sodium, magnesium, aluminium, copper, silver, gold and mercury, members of odd series, are exceptions. Only those compounds of the other classes will be noted which have metallic characters. All the systems hitherto studied will be described; as was said above, the thermal method has greatly elucidated the question of the capacity for combination between heteropolar elements.

Compounds of Boron (Borides).

Boron-iron.—This system has recently been investigated by Hannesen.[1] The compound Fe_5B_2 occurs, containing about 7·2 per cent. by weight of boron. Troost and Hautefeuille [2] had previously observed that iron containing about 23 per cent. of boron became very brittle and unworkable. Hannesen's observations only extend to about 8 per cent. of boron. Mixed crystals of iron δ separate from 0 to 1·38 per cent.; from 1·38 to 4 per cent. mixed crystals of iron γ occur, and from 4 to 8·5 per cent. there takes place the primary separation of the compound Fe_5B_2. Along $A\ T$ (Fig. 146), we have the liquidus curve of the mixed crystals δ, and along $B\ T$, that for the γ crystals.

An eutectic occurs at B for 4 per cent. of boron, and then the curve rises from 1160° to a maximum at 1,351° which is the melting point of the compound.

The behaviour of boron with iron is in many respects analogous to that of carbon.

Boron-nickel.—These alloys have been investigated thermally by Giebelhausen,[3] who observed the formation of four compounds, namely, Ni_2B, Ni_3B_2, NiB and Ni_2B_3. The

[1] *Zeit. anorg. Chem.*, **89**, 287 (1914).
[2] *C. R.*, **81**, 1263 (1875).
[3] *Zeit. anorg. Chem.*, **91**, 257 (1915).

diagram is shown in Fig. 147. Up to 8·5 per cent. of boron, the alloys consist of nickel and the compound Ni_2B. The maximum for this compound is at 1225° and 8·56 per cent. by weight of boron. Ni_2B crystallises only after super-cooling. At about 1165° and 11 per cent. of boron, Ni_3B_2 separates, while at 1125° and 15·8 per cent., NiB is formed. Above 15·8 per cent. of boron, a new species of acicular crystals separates surrounded by the compound

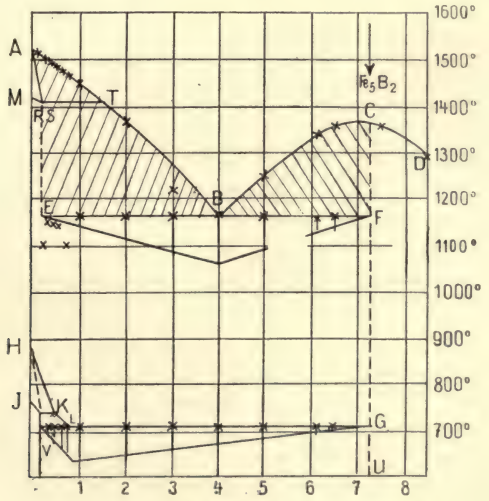

FIG. 146.

NiB. Giebelhausen gives to these new crystals the formula Ni_2B_3. It should be mentioned that the arrest due to secondary crystallisation dies out at 20 per cent. of boron, while the compound Ni_2B_3 would demand 21·8 per cent.

Alloys containing pure nickel have magnetic properties. The compounds are non-magnetic. The hardness of the compound Ni_2B is less than that of quartz. The compounds richer in boron are, perhaps, a little harder, though not so hard as topaz.

Compounds of Carbon (Carbides).

Copper, silver and gold form compounds with carbon of the general formula $R_2C_2 . H_2O$ (where R = Cu, Ag, Au). Such carbides, however, are not of a metallic nature. They are unstable and explosive.

Beryllium, calcium, strontium, barium and magnesium form chemical combinations with carbon which are of great

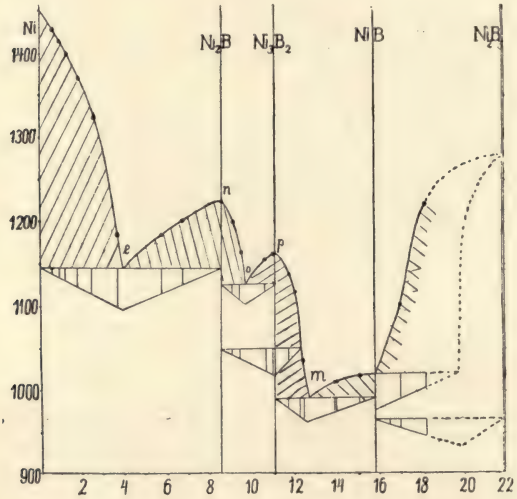

Fig. 147

theoretical and practical importance, but do not display true metallic characters. Mercury also forms an explosive compound of the formula $HgC_2 . H_2O$.

Carbon-boron.—A carbide of the formula B_6C was obtained by Joly (1893) and by Moissan (1894). This carbide is a black crystalline substance of specific gravity 2·51.

Carbon-aluminium.—A carbide of the formula Al_4C_3 was prepared by Moissan (1894) by melting kaolin with carbon

in the electric furnace and by direct combination of aluminium and carbon. In its properties this compound approaches the carbides of the alkaline earth metals.

Carbon-titanium.—The compound TiC was obtained by Moissan in 1895. It is a crystalline substance of specific gravity 4·25 which does not act on steam even at 700°.

Carbon-vanadium.—Alloys of carbon and vanadium are easily obtained in the electric furnace. Moissan obtained in 1896 a carbide with 18·98 per cent. of carbon corresponding to the formula VC.

Carbon-chromium.—Moissan (1894) by heating chromium with carbon in the electric furnace, obtained the compound Cr_3C_2, whose existence, however, is not yet confirmed.

Carbon-molybdenum.—Moissan (1895) obtained a carbide of the formula Mo_2C by heating molybdenum oxide with carbon in the electric furnace.

Carbon-tungsten.—According to Moissan, tungsten combines with carbon at the temperature of the electric furnace, forming the compound W_2C which contains 3·16 per cent. of carbon. Williams has described another carbide, more infusible than the preceding, of the formula WC. According to Böhm (1907), it is formed with difficulty, and he plainly throws doubt on its existence.

Carbon-uranium.—Moissan by heating uranium oxide with carbon obtained from sugar, obtained a carbide of metallic appearance of the probable formula U_2C_3. The same compound was obtained by heating metallic uranium with carbon.

Carbon-manganese. — Troost and Hautefeuille (1875) reported the existence of the carbide Mn_3C which is formed with great development of heat. Moissan (1898) and Leroux (1898) subsequently prepared this carbide. More recently Stadeler [1] studied the system both thermally and microscopically. This investigation is of particular interest from a metallurgical standpoint, particularly since the introduc-

[1] *Metall.*, **5**, 260 (1908).

tion of manganese steels. Up to about 7 per cent. of carbon, the two components form mixed crystals; at 6·72 per cent. of carbon, the carbide Mn_3C separates. The melting point of manganese is raised by carbon up to 1280°, and a continuous series of mixed crystals is formed up to 4 per cent. of carbon; the curve then descends to 1217°, which is the melting point of the carbide.

A complete discussion of the system as far as it is known at present has been made by Guertler.[1]

Carbon-iron.—The alloys of iron with carbon are of the greatest historical importance both in theory and practice. It is not possible to allude here, even in passing, to the properties of the various iron-carbon alloys or to describe the system iron-carbon as developed recently by the application of the principles of the phase rule. The subject is beyond the limits of the present work.[2] The existence of various modifications of iron, all with different physical properties, complicates the study of the system. The two elements, which form isomorphous mixtures, also combine chemically forming the compound called *cementite* which has the formula Fe_3C. The diagram has been discussed on the principles of the phase rule by Roozeboom.[3]

Carbon-nickel.—Ruff and Martin (1912) have reported the existence of a carbide of the formula Ni_2C. Beyond this nothing certain can be stated.

Compounds of Silicon (Silicides).

Silicon-lithium.—Moissan (1902—1903) prepared a silicide of the composition Li_2Si or Li_6Si_2 by direct combination of the two elements. This is the only silicide of the alkali metals known.

Silicon-copper.—Copper forms with silicon the compounds

[1] *Métallographie*, Vol. I., Part II., pp. 8 *et seq.* (1913).

[2] Guertler has devoted one volume of his *Métallographie* to these alloys. His account is the most complete and accurate which we possess at present of the subject.

[3] *Zeit. phys. Chem.*, **34**, 437 (1900); *cf.* also *Contrib. à l'Etude des Alliages*, p. 326 *et seq.*

Cu_3Si and $Cu_{19}Si_4$, the latter of which is to be reckoned as doubtful. The system has been studied by Rudolfi[1] and Vigouroux.[2] De Chalmet [3] had previously reported a compound Cu_2Si, and Lebeau,[4] Cu_4Si. The diagram is given in Fig. 148. From ·98 to 2·93 per cent. of silicon, mixed crystals are formed. At 849°, mixed crystals, *a*, are in equilibrium

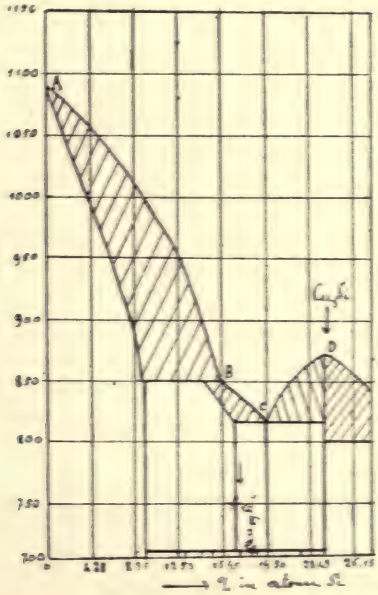

FIG. 148.

with a second species of mixed crystal, *b*, and with the melt *B*. From 7·34 to 8·3 per cent., this second series of mixed crystals occurs. At about 860° and 12·95 per cent. of silicon, the compound Cu_3Si separates. Two reactions occur in the crystalline conglomerates; at 780 to 815°, the second species

[1] *Zeit. anorg. Chem.*, **53**, 216 (1907).
[2] *C. R.*, **123**, 318 (1896).
[3] *J. Am. C. S.* **18**, 95 (1896).
[4] *C. R.*, **141**, 889 (1905).

of mixed crystal breaks up into the first species and a third species richer in silicon. At 710°, the latter species of mixed crystal decomposes, forming the first species and another kind of crystal which is the supposed compound $Cu_{19}Si_4$. Rudolfi states that the compound Cu_2Si reported by Vigouroux and De Chalmet corresponds to the eutectic *E* (not shown on the diagram) and the compound Cu_4Si, to the eutectic *C*.

The alloys of silicon and copper are very brittle; from 8 to 100 per cent. of silicon they are easily powdered. The hardness increases with the silicon content. The colour varies from red and yellow to grey. Alloys containing small quantities of silicon—6·25 to 25 per cent.—are easily oxidised.

Silicon-magnesium.—A silicide of the formula Mg_2Si is known and was prepared by Wöhler in 1858. Gattermann (1889) obtained this compound by the action of magnesium on silicon. Winkler (1890), Vigouroux (1897), Moissan and Smiles (1902) and Lebeau (1908) have successively studied this silicide, which crystallises in greyish octahedra.

Silicon-barium.—A silicide, $BaSi_2$, exists. Jacobs (1900) obtained a silicide by melting barium carbonate or oxide with silica in an electric furnace. Goldschmidt (1908) prepared this silicide industrially together with iron silicide. It has a greyish colour.

Silicon-strontium.—The silicide, $SrSi_2$, was obtained by Jacobs (1900) by the same method as was described for barium silicide.

Silicon-calcium.—The compound $CaSi_2$ probably exists. The system has been studied by Tammann [1] and its diagram is given in Fig. 149. Arrests are noted at 990° from 38 to 82 per cent. of silicon; the maximal arrest, at 60 per cent. of silicon, corresponds to the compound. The formula given is, however, not very well established since the reaction is never completed and Tammann was unable to note the duration

[1] *Zeit. anorg. Chem.*, **62**, 80 (1909).

of the eutectic crystallisation at 803° on account of the small heat of fusion of calcium.

Alloys from 91 to 60 per cent. of silicon are slowly attacked by dilute acids, caustic alkalies and ammonia; the alloys from 38 to 52 per cent. of silicon are strongly attacked by these reagents.

Silicon-cerium.—A compound CeSi probably occurs, but the formula is not well authenticated. The system has

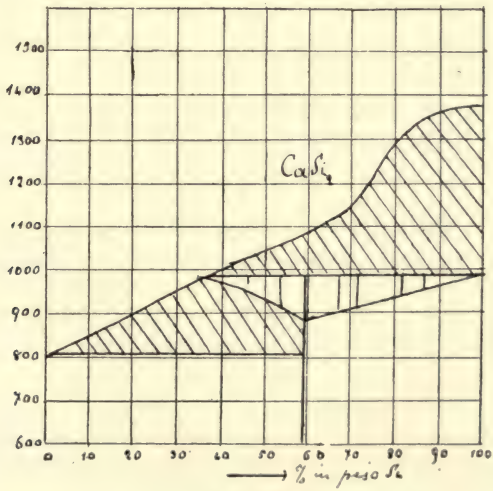

FIG. 149.

been studied by Vogel,[1] but only up to 70 per cent. of cerium. Combination takes place at high temperatures with great evolution of heat. As the diagram (Fig. 150) shows, a compound is formed at 1530° and 16·4 per cent. by weight of silicon. The existence of the compound is also demonstrated by microscopical examination. The alloys are stable in air and unattacked by ordinary chemical reagents. They are hard and brittle.

[1] *Zeit. anorg. Chem.*, **84**, 323 (1914).

Silicon-titanium.—Moissan, in 1895, by the action of silicon on titanic acid in the electric furnace, obtained a compound of the two elements. Two silicides exist, Ti_2Si and $TiSi_2$. The first was obtained by Levy (1895) by allowing gaseous titanium chloride to act on amorphous silicon heated to redness; the second was prepared by Hönigschmidt by a thermite method.

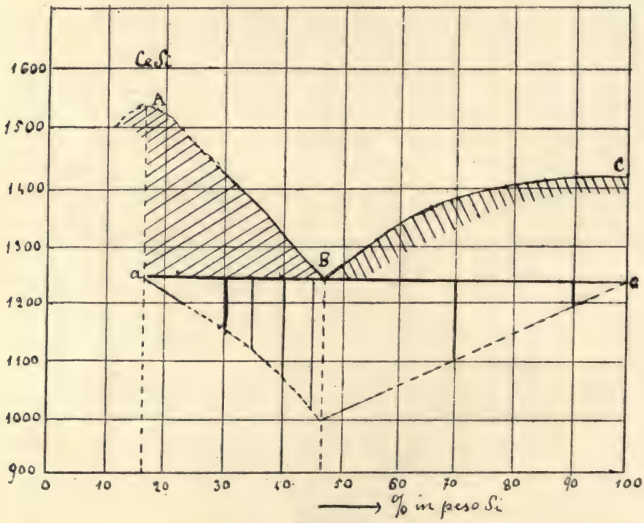

FIG. 150.

$TiSi_2$ crystallises in tetragonal pyramids of an iron grey colour; it is not oxidised in air and is unattacked by mineral acids except hydrofluoric acid.

Silicon-zirconium.—The silicide, $ZrSi_2$, prepared by Hönigschmidt (1906) and Wedekind (1900) is known. $ZrSi_2$ crystallises in rhombs and is stable in air. Wedekind (1910) obtained a colloidal solution of this silicide.

Silicon-thorium.—Hönigschmidt (1906) obtained $ThSi_2$ by action of silicon on thorium oxide in the electric furnace in

the presence of aluminium. It crystallises in dark grey lamellæ.

Silicon-vanadium.—Moissan and Holt,[1] in reducing vanadium oxide with silicon, believed they obtained the compounds V_2Si and VSi_2. The system has since been studied by Giebelhausen,[2] who observed a maximum at 1655° and

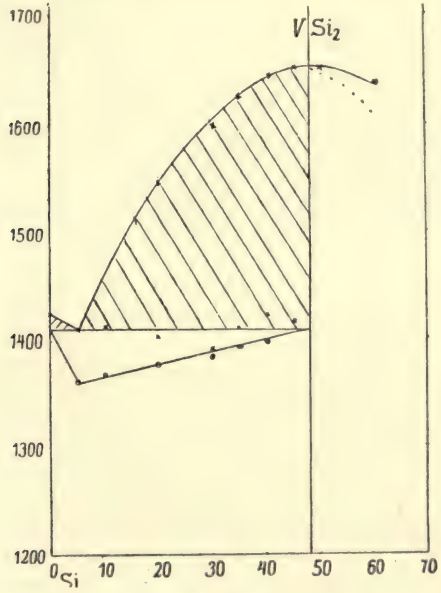

FIG. 151.

47·5 per cent. of vanadium (see Fig. 151). This corresponds to the compound VSi_2. The compound forms mixed crystals with vanadium but not with silicon. These alloys are very brittle; the long needles of the compound are readily separated by simple rubbing. It is hard enough to scratch silicon.

[1] *C. R.*, **135**, 78 and 493 (1902).
[2] *Zeit. anorg. Chem.*, **91**, 251 (1915).

Silicon-tantalum.—A silicide $TaSi_2$ is known; it was prepared by Hönigschmidt (1907) by a thermite method, but not in the pure state.

Silicon-chromium.—Four compounds of these elements are known, namely, Cr_3Si, Cr_2Si, Cr_2Si_3 and $CrSi_2$. They have been studied by Moissan (1895), Zettel (1898), Lebeau (1903), and Vigouroux (1907). These silicides are all crystalline. $CrSi_2$ crystallises in greyish needles having a metallic lustre.

Silicon-molybdenum.—The compounds formed by these elements are Mo_2Si_3 and $MoSi_2$. The first was obtained by Vigouroux (1899), the second by Hönigschmidt (1907). Moissan (1895) had already observed that molybdenum and silicon could combine.

Silicon-tungsten.—The two silicides W_2Si_3 and WSi_2 have been obtained by Vigouroux (1898), Defacqz (1907), and Hönigschmidt (1907). They are grey in colour.

Silicon-uranium.—A compound USi_2 was obtained by Defacqz in 1908 by a thermite method. It is a metallic powder consisting of microscopic cubes.

Silicon-manganese.—These alloys have been studied by Vigouroux,[1] Carnot and Goutal [2] and by P. Lebeau.[3] The last mentioned reports the formation of the compounds Mn_2Si, MnSi and $MnSi_2$. Actually, however, only Mn_2Si and MnSi are formed. A systematic study of the system was made by Doerinckel,[4] whose diagram is reproduced in Fig. 152.

The melting point of manganese is lowered by addition of silicon, and from melts with 0 to 10 per cent. by weight of silicon, mixed crystals containing silicon separate. Between 10 and 30 per cent. of silicon, the fusion curve shows a maximum at about 21·3 per cent. of silicon and 1316°. This corresponds to the compound Mn_2Si. Between 30 to 50 per

[1] *Ann. Chim. Phys.*, (7), **12**, 153 (1896); *C. R.*, **141**, 722 (1905).
[2] *Ann. des Mines*, (9), **18**, 271 (1900).
[3] *C. R.*, **136**, I., 89, 231 (1903); *Bull. Soc. Chim.* (3), **29**, 185 (1903); *Ann. Chim. Phys.* (8), I., 553 (1904).
[4] *Zeit. anorg. Chem.*, **50**, 119 (1906).

cent. of silicon, another maximum occurs at 33·75 per cent. and 1280°, indicating the existence of MnSi. It is probable that at 45 to 50 per cent. silicon and about 1165°, the fusion curve passes through a maximum, either free or obscured, and the author concludes that this would correspond to the compound $MnSi_2$.

Silicon-iron.—This system was studied by Guertler and Tammann,[1] who observed the formation of the compounds Fe_2Si and FeSi. The diagram is shown in Fig. 153. The first compound separates at about 1240° and 33 per cent. of

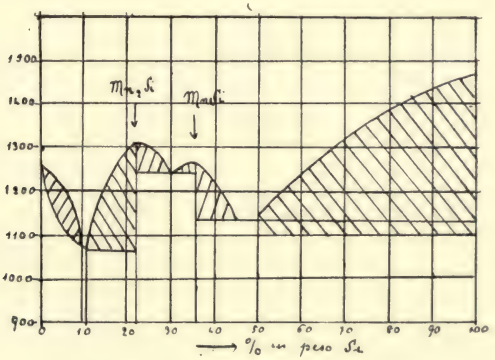

FIG. 152.

silicon, the second at about 50 per cent. and 1443°. From the maximum the curve falls to an eutectic at 76 per cent. silicon. Mixed crystals of iron and the first compound are formed up to 33 per cent. of silicon.

The hardness of these alloys diminishes as the silicon content increases. The compound FeSi is a little less hard than silicon. Fe_2Si is as hard as apatite. The alloys behave in different ways when treated with acids and alkalies. Thus, caustic potash attacks silicon strongly, but the two compounds and iron very slightly. Hydrochloric

[1] *Zeit. anorg. Chem.*, **47**, 163 (1907).

acid acts vigorously on iron, only slightly attacks Fe_2Si and is almost without action on FeSi and silicon.

Silicon-cobalt.—This system has been studied by Levkonja.[1] Four compounds are formed, namely, Co_2Si, CoSi, $CoSi_2$ and Co_3Si_2. The curve is shown in Fig. 154. Three of the compounds give maxima. The first separates at 1327° and 19·5 per cent. by weight of silicon and shows a second thermal effect at 1204°. Between 19·4 per cent. and

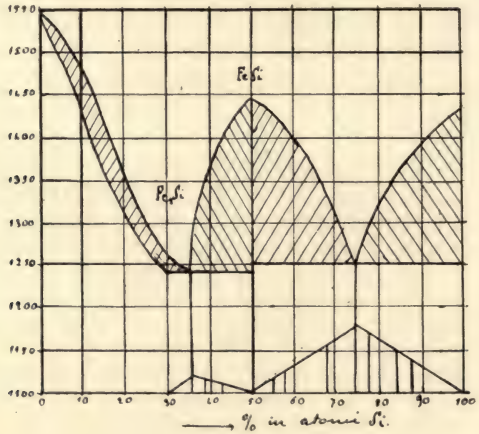

FIG. 153.

32·5 per cent., there occurs another thermal effect with slight super-cooling below 1250°. The maximal arrest is at about 24·8 per cent. of silicon. At this point the compound Co_3Si_2 separates. A second maximum is found at 1395° and 32·5 per cent. of silicon; it corresponds to the compound CoSi. In the alloys between 32·5 and 49 per cent. of silicon, the CoSi of primary separation reacts at 1277° with the melt *F*, forming the compound $CoSi_2$. The third and last maximum is at 1310° and 59 per cent. of silicon.

Magnetic properties are observed in the alloys rich in

[1] *Zeit. anorg. Chem.*, **59**, 327 (1908).

cobalt, particularly in those containing less than 19 per cent. of silicon.

Silicon-nickel.—The system was studied by Guertler and Tammann,[1] who revealed the formation of five compounds, Ni_3Si, Ni_2Si, Ni_3Si_2, NiSi and Ni_2Si_3. Two of these compounds are indicated by distinct maxima. One of these is at

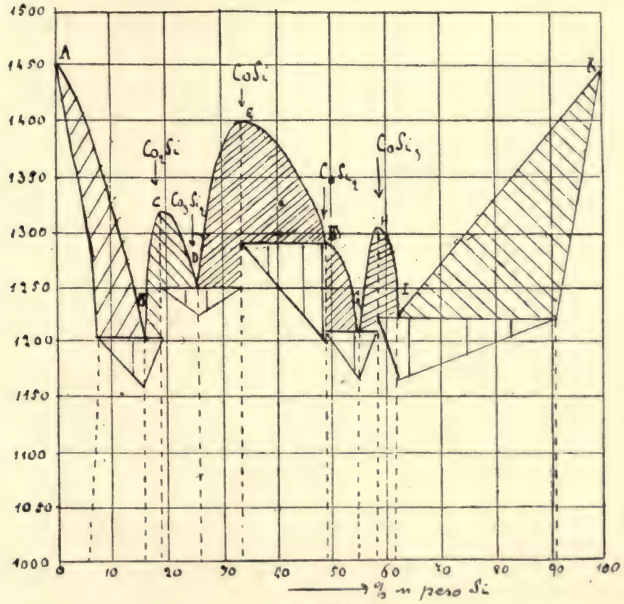

FIG. 154.

about 1309° and 33·3 per cent. of silicon, and corresponds to the compound Ni_2Si. This compound forms a series of mixed crystals with nickel, having a gap from 11·6 to 27·6 per cent. of silicon. Only those alloys from 27·6 to 33·3 per cent. of silicon, however, have a homogeneous structure. Those with less than 27·6 per cent. undergo further transformation below the eutectic temperature, 1150°, so that their primary

[1] *Zeit. anorg. Chem.*, **49**, 93 (1906).

structure is altered. The structure of alloys from 11·6 to 27·6 per cent. varies according as the crystallisation occurs quickly or slowly ; in the former case the melt crystallises, in the latter case a new species of mixed crystals of composition Ni_3Si is formed.

The second maximum, which occurs at about 1000° and

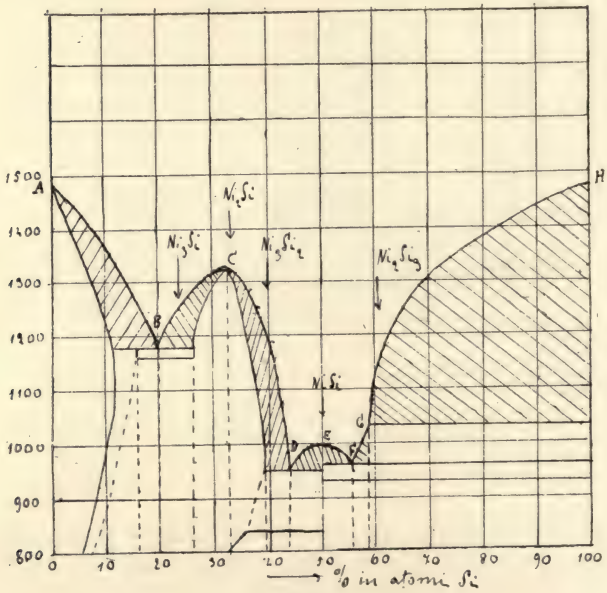

FIG. 155.

49·7 per cent. of silicon, corresponds to the compound NiSi. If the melts from 33·5 to 50 per cent. silicon are cooled quickly, the compound Ni_3Si_2 separates at 40 per cent., while the excess of nickel remains as Ni_2Si. The formation of this compound is accompanied by a super-cooling of 10° to 25°. At 1017° and about 59 per cent. of silicon, there is a thermal effect ; a part of the separated silicon reacts with the melt

of composition *G*, giving rise to a new compound to which the formula Ni_2Si_3 may be given. At 950° and about 60 per cent. of silicon there is a thermal effect which can be interpreted as a polymorphic transformation of this compound.

Alloys up to 22 per cent. of silicon are tough. At higher concentrations they become more brittle. They are similar to nickel in colour up to 15 per cent. of silicon, but thereafter tend to be yellowish, particularly the compound Ni_3Si ; the 33 per cent. alloy is grey, the 40 per cent., reddish, and the 50 per cent., again grey. The 55 per cent. alloy is greyish violet and the alloy with over 70 per cent. of silicon has the grey colour of that element.

Alloys cooled slowly show a minimum of hardness at about 15 per cent. of silicon. With higher silicon contents there is no difference between alloys cooled slowly and those cooled quickly.

Silicon-ruthenium.—Moissan and Manchot (1903) obtained a compound, RuSi, by melting the components in an electric furnace. It crystallises in very hard prisms.

Silicon-platinum.—Two compounds, Pt_2Si and PtSi, are known and were prepared in a pure state by Vigouroux (1896—1897) and by Lebeau (1907). The former compound is white, crystalline and very hard ; the latter compound crystallises in silvery prisms.

Silicon-palladium.—P. Lebeau and J. Jolibois (1908) by union of the two elements obtained the compounds Pd_2Si and PdSi. The union of these elements occurs with evolution of heat at a temperature of about 600°. Both compounds are dark grey in colour.

Phosphides.

Phosphorus-copper.—Copper and phosphorus form the compound Cu_3P. The system has been studied by Heyn and Bauer.[1] The diagram is seen in Fig. 156. At a temperature

[1] *Zeit. anorg. Chem.*, **52**, 131 (1907).

of 1022° and at 14·1 per cent. by weight of phosphorus, arrests are noted which correspond to the compound Cu_3P; the presence of this compound has also been demonstrated by measurements of specific gravity and electrolytic potential. The alloys which have a concentration greater than 14 per cent. of phosphorus solidify with the formation of mixed crystals; from measures of differences of electrolytic potential it appears that they are formed of the compound Cu_3P and a second compound Cu_5P_2.

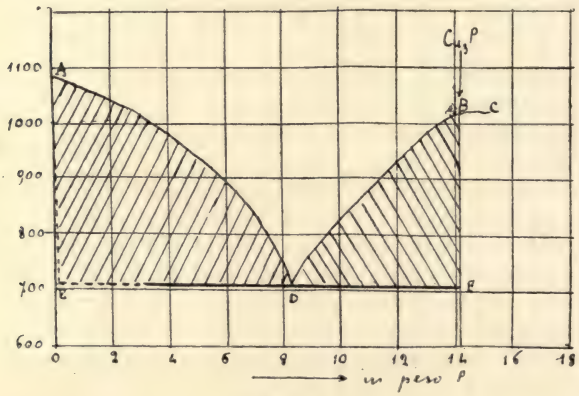

FIG. 156.

Heyn and Bauer could not obtain alloys with more than 15 per cent. of phosphorus, since with rise of temperature alloys richer in phosphorus lose this element by volatilisation. At 1100° the limit *C* is at 14·1 per cent.

Addition of phosphorus increases the hardness of copper.

Phosphorus-silver.—The existence of phosphides of silver is probable, but their composition is not exactly known. Schrötter (1849) obtained a phosphide to which he gave the formula Ag_3P_2; Granger (1898) obtained a phosphide Ag_2P, and Emmerling (1879) reported a compound AgP.

Phosphorus-gold.—Considerable doubt exists as to the

phosphides of gold. Cavazzi (1886) obtained a compound AuP, Schrötter (1849), a compound Au_2P_3, and Granger (1898) observed the formation at 400° of a compound Au_3P_4.

The solubility of phosphorus in gold is diminished at high temperatures.

Phosphorus-magnesium.—The existence of the compound Mg_3P_2, reported by Blunt in 1865, by Parkinson (1867), and Gautier (1899) is probable. Granger, however, believes that the compound Mg_2P_3 is formed.

Phosphorus-zinc.—The compound Zn_3P_2 probably occurs, as reported by Hovsleff (1856), Renault (1866), Schrötter (1873), Emmerling (1879), and Jolibois (1908). The last named and Hovsleff also mention the compound ZnP_2 and Renault the compounds Zn_3P_4 and ZnP_6.

Phosphorus-cadmium.—Cadmium and phosphorus probably combine. Vigier (1861) and Renault (1873) report two compounds, Cd_3P_2 and CdP_2. Emmerling (1879) mentions a phosphide which approximated to the formula Cd_2P.

Phosphorus-mercury.—These elements combine, according to Granger (1892), to form a compound to which he gives one of the formulæ Hg_3P_4 or Hg_3P_6.

Phosphorus-tin.—Phosphorus and tin combine together forming a compound with between 15 and 16 per cent. of phosphorus. Stead (1897) and Campbell (1902) have given the formula as Sn_3P_2, while Jolibois (1909) assigned Sn_4P_3 to the compound. According to the last named, Sn_4P_3 should give rise at 415° to a compound SnP_3, corresponding to 40 per cent. of phosphorus. On these data, Guertler [1] has constructed a fusion diagram for the system.

Phosphorus-bismuth.—The existence of the compounds BiP and BiP_2 has been reported by Cavazzi (1884).

Phosphorus-chromium.—Phosphorus forms in all probability the compound CrP with chromium; it was obtained by Rose (1832), Martins and Maronneau (1900).

[1] Guertler: *Metall.*, **1**, p. 917.

Phosphorus-tungsten.—The compounds formed by the combination of these elements were investigated by Defacqz (1900—1901), who reports compounds having the formulæ WP and WP_2 respectively; they are not, however, well authenticated.

Phosphorus-manganese.—The compounds MnP and Mn_5P_2 are known. The system has been investigated by Zemczuzny and Efremoff,[1] and its diagram is given in Fig. 158. Two

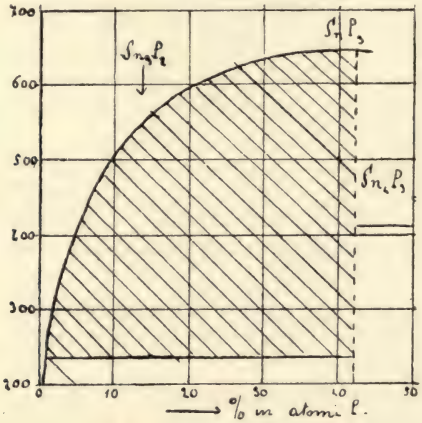

FIG. 157.

maxima and two eutectic points are exhibited. At 1390° and 28·57 per cent. of phosphorus, the compound Mn_5P_2 separates. On the cooling curves, eutectic arrests occur at 964°. Along the branch from 40 to 50 per cent. of phosphorus, solid solutions are formed with a limiting concentration of 44 per cent. phosphorus. The fusion curve could only be traced up to 47 per cent. of phosphorus, because beyond this concentration the phosphorus ignited. This arises from the circumstance that the compound is rather unstable and partially dissociates at high temperatures.

[1] *Zeit. anorg. Chem.*, **57**, 247 (1908).

This compound, from analogy with the corresponding derivatives of antimony and arsenic, has been given the formula MnP. From 10 per cent. of phosphorus the alloys have magnetic properties, which reach a maximum intensity at 28 to 30 per cent. of phosphorus (Mn_5P_2) and then decrease in intensity.

Phosphorus-iron.—Iron and phosphorus form the compounds Fe_3P and Fe_2P. The system has been studied ther-

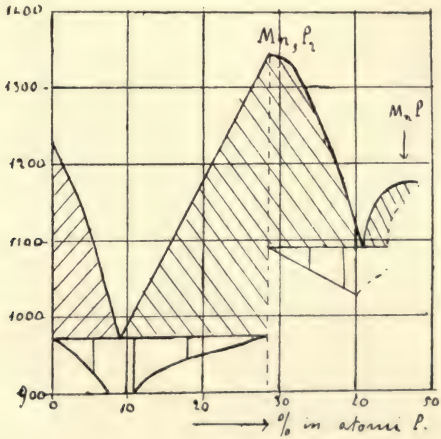

FIG. 158.

mally up to a concentration of about 32 per cent. of phosphorus by Saklatvalla,[1] by Gercke,[2] and by Konstantinoff.[3] In the diagram (Fig. 159) the first compound is indicated by a discontinuity in the curve at about 1135° and 25 per cent. of phosphorus. The second compound gives a maximum at 1350° and 33·3 per cent. of phosphorus. By addition of phosphorus the melting point of iron is lowered to 1020° at 17 per cent. of phosphorus. Phosphorus forms

[1] *Métall.*, 5, 321 (1908).
[2] *Ibid.*, 604.
[3] *Chem. Centr.*, I., 601, 1920 (1910)

solid solutions with iron γ; the limit of saturation is at about 3 per cent. of phosphorus. At 610° Gercke noticed a thermal effect, which he attributed to a decomposition of these mixed crystals.

Le Chatelier and Wologdine (1909) reported the existence of two phosphides, FeP_2 and Fe_2P_3.

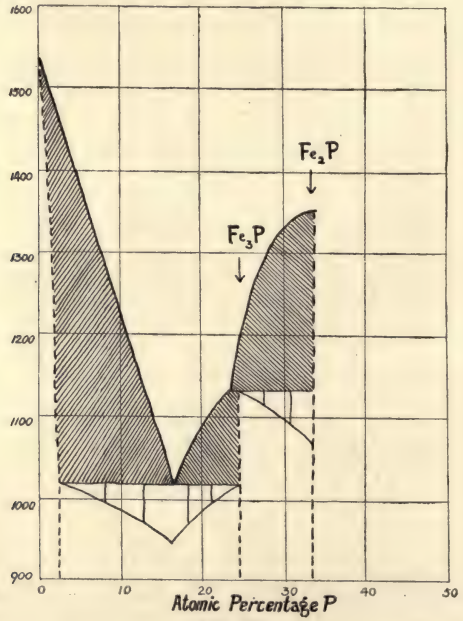

FIG. 159.

Phosphorus-cobalt.—The compound Co_2P occurs. The system has been investigated up to 40 per cent. of phosphorus by Zemczuzny and Schepeleff.[1] The diagram (Fig. 160) shows that the compound Co_2P, which melts without dissociation, is formed at 33·3 per cent. of phosphorus and 1386°. On the cooling curves two other arrests

[1] *Zeit. anorg. Chem.*, **64**, 251 (1909).

are noted, one at 1022°, due to eutectic crystallisation, and the other at 920° and 8 to 33·3 per cent. of phosphorus, due to the formation of a modification of the compound. The compound is harder than cobalt and has magnetic properties, though to a smaller extent than cobalt and the intermediate alloys.

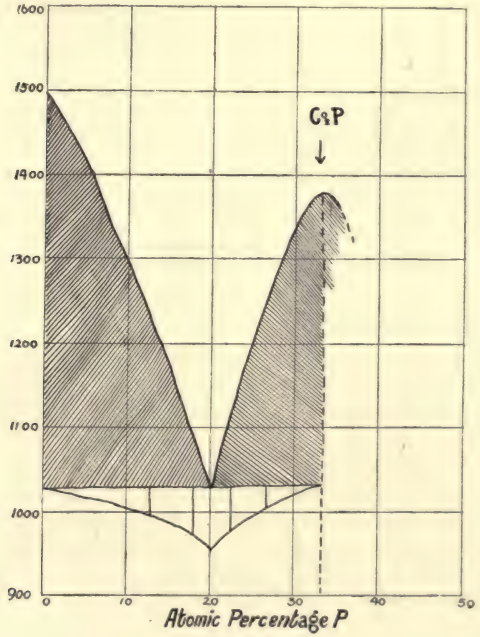

FIG. 160.

Phosphorus-nickel.—Phosphorus forms with nickel the compounds Ni_3P, Ni_5P_2 and Ni_2P. The system has been investigated by Konstantinoff [1] up to a concentration of 35·5 per cent. phosphorus, and the diagram is shown in Fig. 161. The melting point of nickel is lowered by addition of phosphorus. The eutectic point is found at 880° and 19 per

[1] *Zeit. anorg. Chem.*, **60**, 410 (1908).

cent. of phosphorus. Along *B C* the compound Ni_3P separates ; at 23 per cent. of phosphorus and 960°, it decomposes with formation of Ni_5P_2. The reaction, however, does not proceed to completion. The maximum for this compound on the curve is at 1182° and 28·3 per cent. of phosphorus. A series of arrests at 1025° indicate a modification,

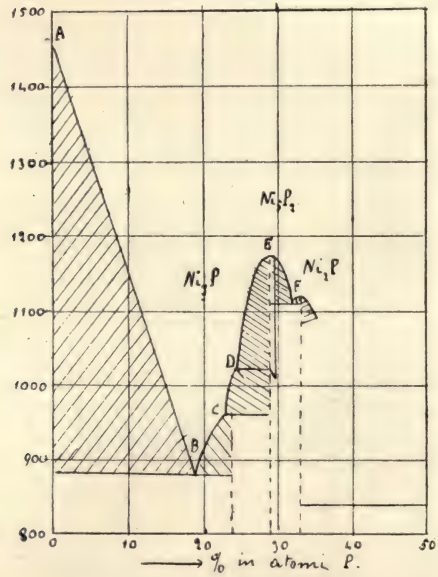

FIG. 161.

α, of this compound. At concentrations above 28·4, these arrest points are lowered from 1025° to 1000°. The maximal arrest occurs at 29·5 per cent. of phosphorus, and thereafter the arrests decrease until the ordinate of the compound Ni_2P is reached. The compound Ni_5P_2 in its β form gives rise to solid solutions, while the α form does not. In the transformation from the β to the α form the solid solutions split up into α Ni_5P_2 and Ni_2P. This latter compound,

which separates at 1110°, differs from the compound Ni_5P_2 in colour ; Ni_5P_2 is yellow, while Ni_2P is steel grey. Ni_2P is also distinguished by its long needle-like crystals. At 830°, arrest points occur which probably indicate an eutectic containing a compound richer in phosphorus and unstable at higher temperatures.

Phosphorus-palladium.—According to Schrötter (1849) phosphorus and palladium form a compound PdP_2.

Phosphorus-iridium.—Schrötter (1848) also reports a compound IrP_2.

Phosphorus-platinum.—According to Schrötter the phosphide PtP_2 exists, while Davy obtained phosphides of composition between PtP and Pt_2P. Clarke and Joslin (1883) report the existence of four compounds : Pt_3P_5, PPt_2, PPt, and PPt_2. Granger (1898) heated platinum in phosphorus vapour and obtained PtP_2 and Pt_2P. Pt_3P_5 should be a decomposition product.

Compounds of Arsenic (Arsenides).

Arsenic-copper.—These elements form the compounds Cu_3As and Cu_5As_2. The system has been studied by Hiorns,[1] Hiorns and Lamb,[2] Friedrich [3] and Bengough and Hill (1910).

The curve (Fig. 162) falls from the melting point of pure copper to an eutectic point at 685° and about 20 per cent. of arsenic. Friedrich observed the formation of solid solutions of arsenic in copper up to 4 per cent. of arsenic. The eutectic horizontal reaches as far as 25 per cent. of arsenic which corresponds to the compound Cu_3As. At 26 per cent. of arsenic, another horizontal occurs at 710° which should be due to the formation of the compound Cu_5As_2. According to Guertler [4] this horizontal represents a polymorphic transformation of the compound. It has not been ascertained

[1] *J. Soc. Chem. Ind.*, **28**, 451 (1909).
[2] *Ibid.*
[3] *Metall.*, **2**, 490 (1905).
[4] *Metall.*, Vol. I., Part I.a, p. 842.

whether the two compounds form solid solutions. The existence of the compounds Cu_2As and CuAs is doubtful.

Arsenic-silver.—This system has been investigated by Friedrich[1] up to 25 per cent. of arsenic. It is not certain if the compound Ag_3As is formed. The eutectic point has not been reached. At 528°, however, a horizontal was noted which is probably eutectic.

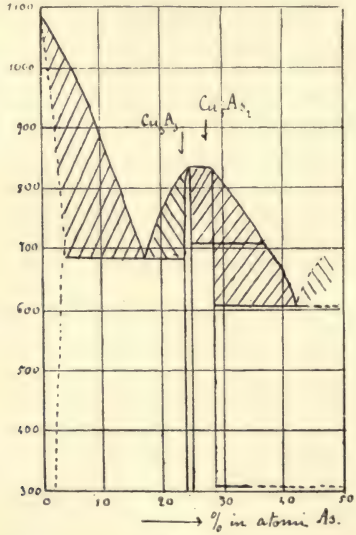

FIG. 162.

Arsenic-gold.—It is not certain if these elements combine with each other. Descamps (1878) obtained an alloy of composition Au_4As_3. Tivoli (1886) prepared a substance AuAs stable below 130°.

Arsenic-magnesium.—These elements combine forming the compound Mg_3As_2 obtained by Parkinson (1867).

Arsenic-zinc.—The compound Zn_3As_2 is probably formed

[1] Friedrich and Leroux, *Metall.*, **3**, 194 (1906).

by the union of these elements. The system was studied thermally by Friedrich and Leroux,[1] and by Arnemann.[2] The data, however, do not go beyond 14 per cent. of arsenic.

Arsenic-cadmium.—Two compounds are known, Cd_3As_2

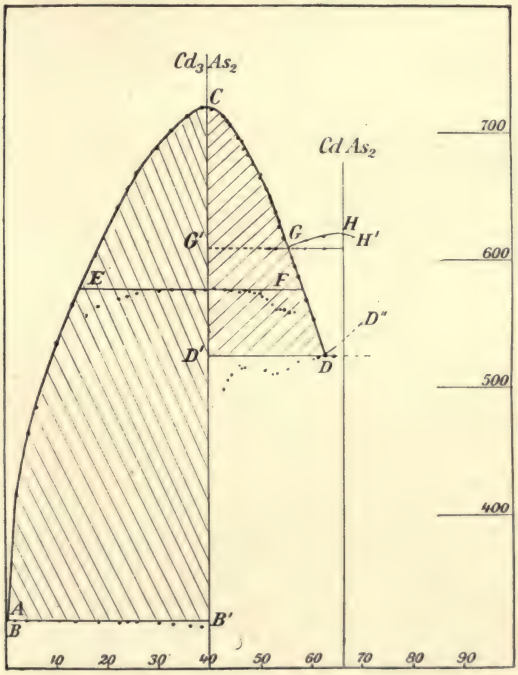

FIG. 163.

and $CdAs_2$. The system was studied up to about 56·4 per cent. of arsenic by Zemczuzny.[3] The two arsenides of cadmium are fairly stable. Cd_3As_2 melts at 721° and $CdAs_2$ at 621° (see Fig. 163). Arsenic is very slightly soluble in

[1] *Metall.*, **3**, 477 (1906).
[2] *Ibid.*, **7**, 201 (1910).
[3] *Chem. Centr.*, 1913, II., 2102, and *Int. Z. Metall.*, **4**, 228 (1913).

molten cadmium, and the melting point of cadmium is only lowered by 1·5° by addition of arsenic.

The cadmium-arsenic alloys have also been studied by De Cesaris,[1] who established thermally the existence of the compound Cd_3As_2.

Arsenic-mercury.—Ramsay [2] prepared an arsenic amalgam by electrolysis of a solution of $AsCl_3$ using a mercury cathode. Vortmann,[3] Partheil and Amort,[4] and Dumesnil [5] also investigated the arsenic amalgams.

The existence of a compound of the formula As_2Hg_3 is probable; it crystallises in yellowish-brown lamellæ which are easily oxidised.

Arsenic-thallium. — It is not certain whether these elements combine with each other. Carstanjen (1867) obtained a soft alloy of the composition Tl_2As.

Arsenic-lead.—These elements probably form a compound Pb_3As_4. The system has been studied thermally up to 34·4 per cent. of arsenic by Friedrich.[6] He noticed the occurrence of two liquid strata, one rich in arsenic and a lower stratum of the compound. An eutectic point was observed at 293°. The data obtained were not sufficiently reliable to enable Friedrich to construct a diagram.

Arsenic-tin.—Two compounds are known, Sn_3As_2 and SnAs. The system was studied up to 50 per cent. of arsenic by Parravano and De Cesaris [7] and by Jolibois and Dupuis.[8] Various compounds of tin and arsenic are described in chemical literature. Spring,[9] by submitting arsenic and tin to high pressure, obtained an arsenide to which he gave the formula Sn_3As_4.

The diagram constructed by Parravano and De Cesaris is

[1] *Rend. Soc. Chim. Ital.*, (2), **4**, 196 (1912).
[2] *J. C. S.*, **55**, 531 (1889).
[3] *Ber.*, **24**, 2764 (1891).
[4] *Arch. Pharm.*, **237**, 126 (1899).
[5] *C. R.*, **152**. 868 (1911).
[6] *Metall.*, **3**, 46 (1906).
[7] *Gazz. Chim. Ital.*, **42**, I., 274 (1912); *R. Acc. Lincei* (5), **20**, 593 (1911).
[8] *C. R.*, **152**, 1312 (1911).
[9] *Ber.*, **16**, 324 (1883).

shown in Fig. 164. The melting point of tin is practically not lowered by addition of arsenic, and the curve rises from that point on the diagram, at first steeply, and then more slowly to the limit reached in the experiment. Three horizontals are found in the diagram which correspond to the compounds mentioned. The region of existence of the compound SnAs is somewhat restricted and the compound is dissociated on fusion.

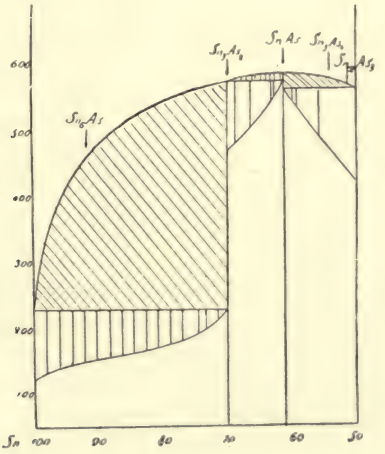

FIG. 164.

Jolibois and Dupuis report the existence of two compounds, Sn_4As_3 and SnAs. The thermal results obtained, however, are not very reliable.

Arsenic-manganese.—The alloys of these elements have been studied by Dieckmann (1911), and by Friedrich and Schoen.[1] Three compounds are formed, Mn_2As, Mn_3As_2 and MnAs.

The fusion diagram is given in Fig. 165 and shows three branches with two eutectics, one at 930° and 17 per cent. of

[1] *Metall.*, **8**, 727 (1911).

arsenic and the other at 870° and 43 per cent. of arsenic. At 1092° and 33·3 per cent. of arsenic, a maximum occurs indicating the separation of the compound Mn_2As. The second maximum is at 930° and corresponds to the compound MnAs. The third compound should be formed at 40 per cent. and 760°. The curve could not be traced beyond 50 per cent. of arsenic on account of the volatility of arsenic.

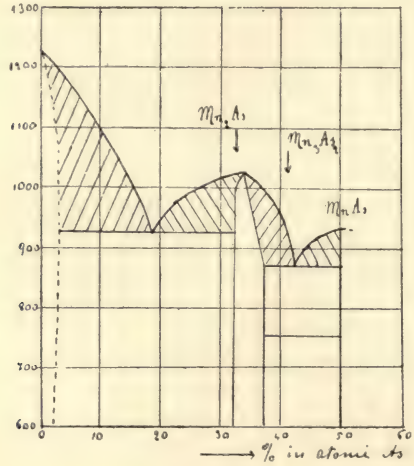

FIG. 165.

A loys between 38 and 48 per cent. of arsenic are magnetisable. Those richer in magnanese, after quick cooling, and those richer in arsenic, after slow cooling.

Arsenic-iron.—This system has been investigated by Friedrich[1] up to about 60 per cent. of arsenic. Up to this concentration, the following compounds occur: Fe_2As, Fe_3As_2, FeAs and Fe_5As_4 (?).

From 1520° (see Fig. 166) the curve falls to an eutectic at 840° between iron and the compound Fe_2As, which latter

[1] *Metall.*, **4**, 131 (1907).

gives rise to a maximum at 920°. At 1030° the compound FeAs separates. Almost as soon as this compound separates, another thermal effect is observed at 1004°, which reaches a maximum near the fusion curve. According to Friedrich, it corresponds to the formation of a compound Fe_5As_4. At 799°, FeAs and Fe_2As react with each other, giving rise to Fe_3As_2.

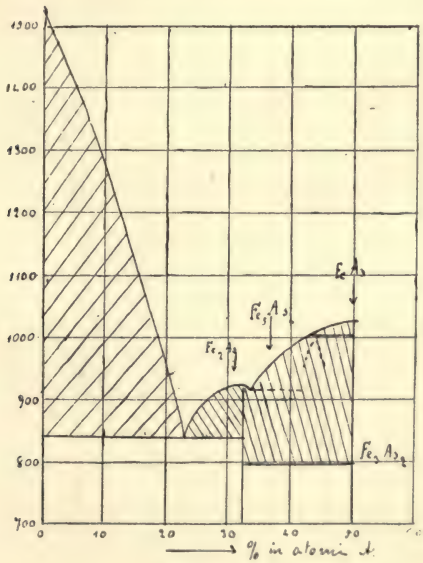

FIG. 166.

Arsenic-cobalt.—The compounds Co_5As_2, Co_2As, Co_3As_2 and CoAs are known. The system has been studied by Ducelliez [1] and Friedrich,[2] who have carried their observations as far as mixtures containing 55 per cent. of arsenic. The compound CoAs corresponds to the maximum which is seen on the diagram (Fig. 167) at about 1175°. The other compounds separate between the maximum and the eutectic

[1] *C. R.*, **147**, 424.
[2] *Metall.*, **5**, 150 (1908).

and give rise to discontinuities with which are associated three horizontals indicating thermal arrests. Co_3As_2 is indicated by a maximal arrest at 1014° and about 37 per cent. of arsenic, Co_2As by one at 960° and 33·3 per cent. of arsenic, and Co_5As_2 by one at 920° and 28 per cent. of arsenic. At 830° another horizontal is observed which is probably due to a transformation of the last compound. Another

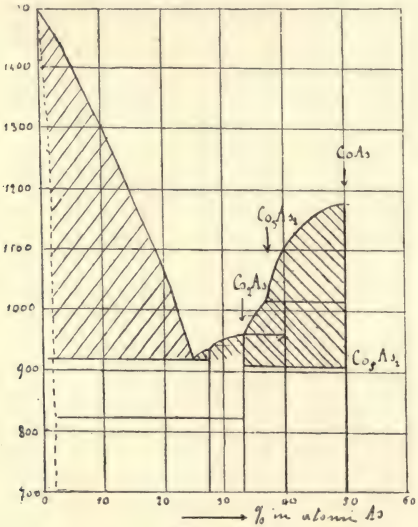

FIG. 167.

horizontal at 910° is probably due to a transformation of Co_3As_2. According to Friedrich, the horizontal at 830° should be attributed to a transformation of Co_2As into another compound.

Arsenic-nickel.—Two compounds are known, namely, Ni_5As_2 and NiAs, whose existence was inferred by Friedrich [1] from a study of the system up to a concentration of about 60 per cent. of arsenic. The two compounds are shown in

[1] *Metall.*, **4**, 207 (1907).

the diagram (Fig. 168) in the form of two maxima, one at 1000° and 28 per cent. of arsenic, and the other at 965° and 50 per cent. of arsenic. At 950° thermal effects are noted which are diagrammatically represented by a bow-shaped curve. According to Friedrich they are due to a new crystalline species which is formed on the one hand from Ni_5As_2 and excess of nickel, while on the other hand Ni_5As_2

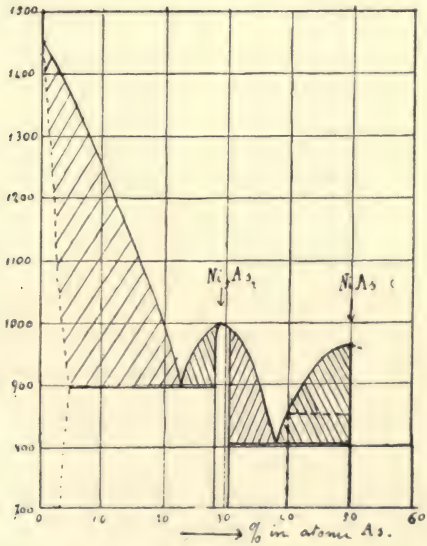

FIG. 168.

is formed directly from the melt with an excess of arsenic. At temperatures between 500° and 600°, transformations are observed in the alloys below the eutectics. A new crystalline species is formed which probably corresponds to the formula Ni_3As_2.

Arsenic-platinum.—The compound Pt_2As_3 is known. The system was studied by Friedrich and Leroux [1] up to a concentration of about 35 per cent. of arsenic. The diagram

[1] *Metall.*, **5**, 148 (1908).

constructed by them is given in Fig. 169. It consists of two branches intersecting in an eutectic point at 599° and about 28 per cent. of arsenic. The eutectic horizontal reaches on the one side as far as pure platinum and on the other as far as the concentration required by the compound Pt_2As_3. Friedrich and Leroux did not obtain the compound $PtAs_2$

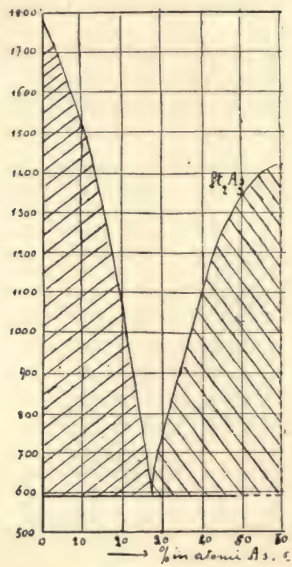

FIG. 169.

prepared by other workers on account of the considerable loss of arsenic which took place from melts containing more than 30 per cent. of that element.

COMPOUNDS OF SULPHUR (SULPHIDES).[1]

Sulphur-rubidium.—Sulphur combines with rubidium, forming the compounds Rb_2S_3, Rb_2S_4, Rb_2S_5 and Rb_2S_6.

[1] The compounds mentioned here are those studied thermally; many well known sulphides are of course omitted; they are described in any modern work on inorganic chemistry.

The system has been studied by Biltz and Wilke-Dörfurt.[1] The curve (Fig. 170) shows only one maximum, which corresponds to the pentasulphide, the other three compounds being marked by discontinuities. Four thermal horizontals between the compounds are also noted. The first compound is formed at 200° and 36 per cent. of sulphur, the second at 160·4° and 42·8 per cent. of sulphur, the third at 230° and 48·3 per cent. of sulphur, and the last at 206° and 53 per cent. of sulphur. The tetrasulphide decomposes below its melting

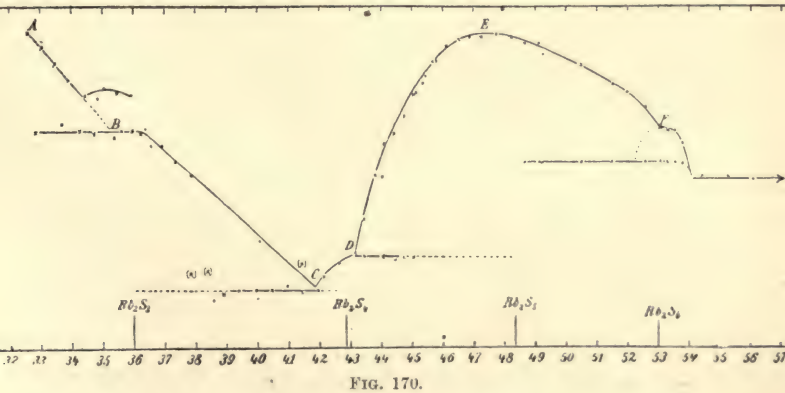

FIG. 170.

point. The hexasulphide is characterised by an obscured maximum between 53 and 54 per cent. There is a rise in temperature of 200° on the fusion curve between the bisulphide and the trisulphide. It cannot be said with certainty whether a third compound is formed from these compounds or whether a polymorphic transformation of the bisulphide occurs. To obtain the crystallisation of the compounds Biltz and Wilke-Dörfurt had recourse to inoculation of the fused mixtures.

The alloys formed varied in colour from red to chestnut red.

[1] *Zeit. anorg. Chem.*, **48**, 314 (1906).

Sulphur-cæsium.—The compounds Cs_2S_2, Cs_2S_3, Ss_2S_4, Cs_2S_5, and Cs_2S_6 are formed by the union of these elements.

This system was also studied by Biltz and Wilke-Dörfurt.[1] The curve (Fig. 171) is similar to that for rubidium-sulphur. It shows a maximum at 37·6 per cent. and 210° and two discontinuities, one at 32·5 per cent. and 160° for the tetrasulphide, and the other at 42 per cent. and 183° for the hexasulphide. The trisulphide has an extended but indeterminate region of existence so that it can only be identified by the change in the eutectic horizontals at 205·5° and 151°.

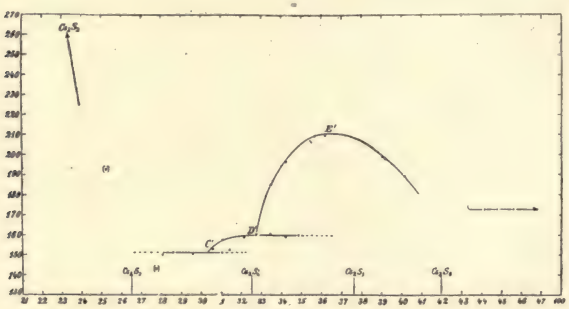

FIG. 171.

As in the preceding system it was necessary to seed the fused mixtures to start crystallisation. The alloys are similar in colour to those of rubidium.

Sulphur-copper.—The compound Cu_2S is formed. The system has been studied by E. Heyn and O. Bauer [2] and by Friedrich (1908). The melting point of the sulphide was found by the first two workers at 1127° and by Friedrich at 1135°. Friedrich also noticed that the liquidus curve was lowered by further addition of sulphur (Fig. 172). On melting sulphur with copper, two liquid layers are formed, as was noticed by Mourlot (1897), and later by Heyn and Bauer.

[1] *Zeit. anorg. Chem.*, **48**, 316 (1906).
[2] *Metall.*, **3**, 76 (1906).

The upper layer contained 85 per cent. of the sulphide, while the lower layer was rich in copper and only contained 9 per cent. of the compound. Solid solutions were not observed to occur.

Sulphur-silver.—The compound Ag_2S occurs. The alloys of silver sulphide and silver have been studied by Rössler (1895), Pélabon [1] and Friedrich and Leroux.[2] Thermal analysis showed that the compound melted at 812° and that at 906° a monotectic horizontal occurred (see Fig. 173). The

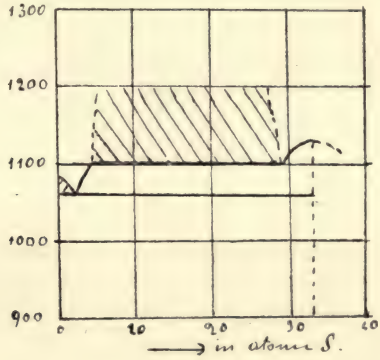

FIG. 172.

occurrence of two liquid layers in the fused state was also observed. Of these liquid strata, the lower contained the sulphide mixed with silver, while the upper contained no free silver. Friedrich and Leroux observed at 175° a transformation of the silver sulphide. It is probable that solid solutions of sulphur in silver occur.

Sulphur-gold.—These elements combine directly with difficulty ; it appears, however, that the compound Au_2S is formed which was obtained by McLaurin (1896).

Sulphur-bismuth.—The compound Bi_2S_3 is known. The

[1] *C. R.*, **143**, 294 (1906).
[2] *Metall.*, 365 (1906).

system has been studied by Aten,[1] and by Pélabon,[2] who reports that at 760° and 50 per cent. a compound BiS separates. The existence of this compound is, however, denied by Aten, who states that the curve from ·1 to 52·4 per cent. of sulphur is simply the fusion curve of a single sulphide containing more sulphur than BiS—probably Bi_2S_3. The study of the system has not been carried beyond 55 per cent. of sulphur because at this concentration the mixture boils at its melting point, *i.e.*, the melting point and boiling point

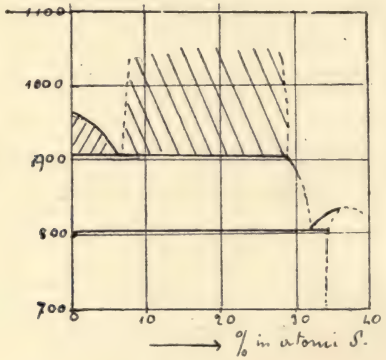

FIG. 173.

curves intersect. The compound Bi_2S_3 is partially dissociated in solution since it produces sulphur vapour.

Sulphur-indium.—The compounds In_2S_3, In_2S, and InS are formed, of which the first two were reported by Thiel (1904) and the last by Thiel and Koelsch (1910).

Sulphur-thallium.—The sulphide Tl_2S exists and, as Bessler (1895) observed, it combines with sulphur. Pélabon[3] has followed the curve of fusion. At 448° and the concentration of the compound a maximum is observed. Between the sulphide and pure thallium two immiscible melts occur.

[1] *Zeit. anorg. Chem.*, **47**, 387 (1905).
[2] *Journ. Ch. Phys.*, **2**, 320 (1904).
[3] *C. R.*, **145**, (118) 1907.

With increase of sulphur the curve falls rapidly from the maximum. At a concentration corresponding to Tl_2S_5 the curve passes through 125°. Pélabon's data are, however, incomplete.

Sulphur-tin.—These elements combine, forming the compound SnS. The system has been studied by Biltz and Mecklenburg.[1] The diagram is given in Fig. 175. The

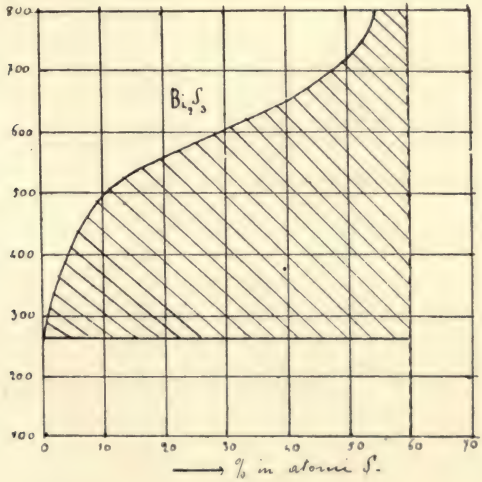

FIG. 174.

compound is formed at 881° at a concentration of 21·6 per cent. of sulphur. From the maximum representing the compound the curve descends on the left, at first rapidly and then slowly, so as to appear almost horizontal, as if to indicate a lack of miscibility in the liquid state. This, however, is not the case as the boiling point curve above 1200° shows. The curve then descends almost vertically to the eutectic point, which is practically coincident with the melting point of tin. The existence of two distinct strata in solid mixtures

[1] *Zeit. anorg. Chem.*, **64**, 231 (1909).

may be noted, due to the great difference in the melting point and specific gravity of the components. The curve on the other side of the maximum descends, but has only been followed for a short distance on account of the volatility of the free sulphur.

Sulphur-lead.—Sulphur and lead form the compound PbS.

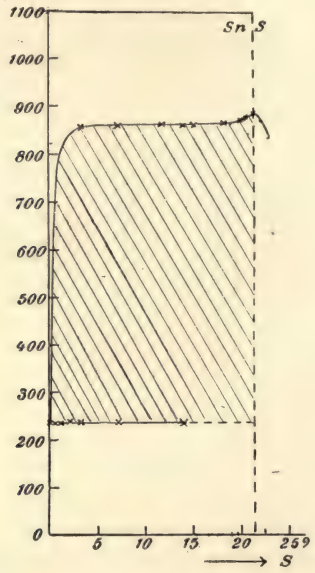

FIG. 175.

The system has been studied by Friedrich and Leroux.[1] From the diagram (Fig. 176) it appears that by addition of sulphur the liquidus curve rises almost vertically. At 1150° a short horizontal tract is noticed. The melting point of the compound is at about 1120°. Two liquid layers are formed.

Sulphur-arsenic.—The two compounds As_2S_2 and As_2S_3

[1] *Metall.*, **2**, 536 (1905).

are known. The former melts at 320° and is dissociated in the fused state ; the latter melts at 310° and is undissociated even at boiling temperature. The system has been studied by Jonker [1] and Borodovsky.[2]

The diagram constructed by Jonker is shown in Fig. 177. It shows that solid solutions do not occur between As_2S_3 and sulphur, which is due to the fact that the liquid mixtures

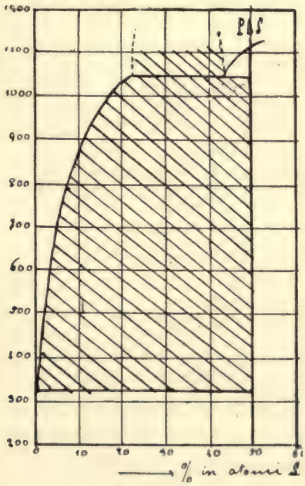

FIG. 176.

are exceedingly viscous. The same is the case between As_2S_2 and sulphur. Jonker has carried out viscosity determinations and has observed that the viscosity diminishes slowly at high temperatures. The existence of other compounds is not certain. As_2S_5 may be formed from 60 to 80 per cent. of sulphur.

Borodovsky's results are not in concordance with those of Jonker. He gives the melting point of As_2S_2 as 308° and

[1] *Zeit. anorg. Chem.*, **62**, 89 (1909).
[2] *Rend. Soc. Chem. di Dorpat*, **14**, 159 (1906).

the eutectic point as 225°. The curve then rises and shows a discontinuity at about 300°.

Sulphur-selenium.—The two components are completely miscible in the liquid state. The existence of the compound Se_2S is doubtful. The system has been studied by Ringer.[1] From his diagram it appears that solid solutions of sulphur in selenium occur up to 13 per cent., and of selenium in

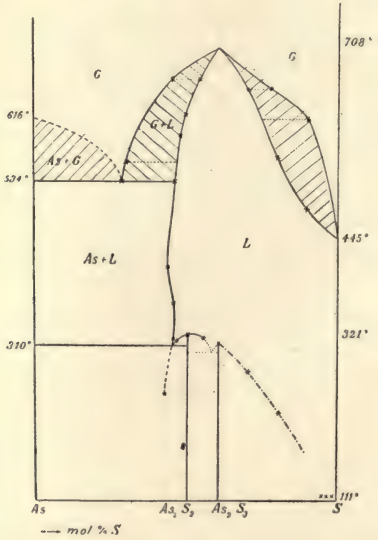

FIG. 177.

monoclinic sulphur up to 27 per cent. The solubility of selenium in rhombic sulphur is but small. An intermediate crystalline species occurs between 18 and 50 per cent.

Sulphur-molybdenum.—The compounds Mo_2S_3 and MoS_2 occur ; they were obtained by Guichard (1900) ; the second is formed by heating the first compound.

Sulphur-manganese.—Manganese combines with sulphur,

[1] *Zeit. anorg. Chem.*, **32**, 202 (1902).

but little is known thermally. The compound MnS is probably formed. The manganese sulphides have been studied by Le Chatelier and Ziegler (1902).

Sulphur-iron.—The compound FeS occurs. The system *iron-iron sulphide* has been studied by Treitschke and Tammann [1] and by Friedrich.[2] These workers deny the existence of compounds between FeS and pure sulphur.

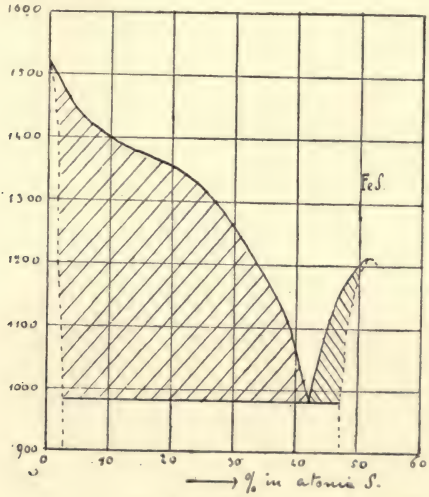

FIG. 178.

The sulphide and sulphur mix in all proportions in the liquid state ; from the liquid mixtures, FeS and iron probably do not crystallise in the pure state, but α Fe absorbs small quantities of FeS (less than 1 per cent.). Whenever small traces of the oxides or silicates of iron are present a lack of miscibility is noticed in the system, and about 60° below the eutectic arrest an arrest is noted which has its maximum at the eutectic composition.

The equilibrium diagram (Fig. 178), due to Tammann and

[1] *Zeit. anorg. Chem.*, **49**, 320 (1906).
[2] *Metall.*, **7**, 257 (1910).

Treitschke, represents the system Fe-FeS in presence of iron oxide. In addition to the lack of miscibility two slackenings are noticed, one at 970° and the other at 910°, with the maximum duration at the eutectic composition. In the presence of oxide of iron the quantities of FeS which dissolve

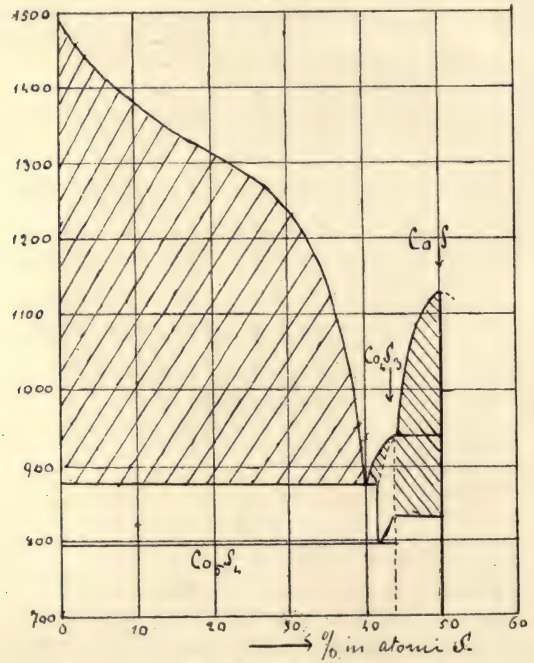

FIG. 179.

in Fe-γ are greater and a lowering of the transformation point into Fe-β is produced. Also, iron sulphide does not show the transformation which, in the absence of oxide, takes place at 298°.

Iron containing sulphur becomes brittle on heating, even when less than ·02 per cent. is present. In the cold it is

brittle with about ·5 per cent. of sulphur. The brittleness is due to the presence of lamellæ of iron sulphide intercalated between the crystals of iron.

Sulphur-cobalt.—According to Friedrich[1] the compounds Co_4S_3, Co_5S_4, Co_6S_3 and CoS are probably formed. The

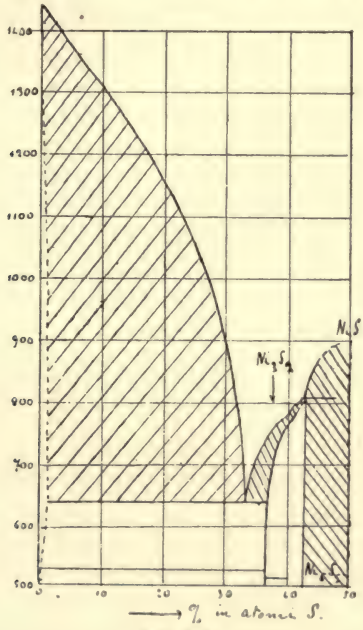

FIG. 180.

existence of the last three is not well authenticated. The curve (Fig. 179) shows an eutectic point at 40 per cent. Although this corresponds to the composition of a compound Co_3S_2, the alloy is really an eutectic mixture, as is revealed by microscopical examination. At 930° a discontinuity occurs on the curve at a concentration corresponding to the formula Co_4S_3. This crystalline species, which is formed at 790°,

[1] *Metall.*, **5**, 212 (1908).

decomposes into another species to which in all probability the formula Co_5S_4 belongs. At about 50 per cent. of sulphur a flattened maximum is observed corresponding to the compound CoS. Solid solutions of sulphur in cobalt do not exist to any measurable extent.

Sulphur-nickel.—The compounds Ni_3S_2, Ni_6S_5 and, probably, NiS occur. The system has been investigated by Bornemann,[1] and the diagram is shown in Fig. 180. From the melting point of nickel the curve falls to an eutectic point at 644°. This point occurs at 33·3 per cent. sulphur, but, as shown by microscopical analysis, no compound occurs. At about 785° and 40 per cent. of sulphur Ni_3S_2 separates ; it decomposes at 532°, giving another crystalline species ; this in turn undergoes a decomposition at 520°, giving a compound with the probable formula Ni_6S_5. The curve was followed by Bornemann up to 45 per cent. of sulphur. In all probability, as Guertler [2] observes, the compound NiS is formed at about 900° and 50 per cent. of sulphur.

Sulphur-palladium.—The sulphide Pd_2S obtained by Schneider [3] and Rössler (1895) exists.

Compounds of Selenium (Selenides).

Selenium-copper.—The system *copper-copper selenide* has been studied by Friedrich and Leroux.[4] The existence of Cu_2Se is revealed. The maximum, as is seen from the diagram (Fig. 181), is at 1113° and 33·3 per cent. of selenium. At 1063° there is an eutectic horizontal which reaches from the composition of the compound to that of pure copper. Friedrich and Leroux report a tendency to the formation of strata. Guertler [5] also reports the existence of a compound CuSe whose melting point would be found to be much lower than that of the first compound.

[1] *Metall.*, **5**, 13 (1908).
[2] *Metallographie*, Vol. I., p. 986.
[3] *Pogg. Ann.*, **141**, 530 (1870).
[4] *Metall.*, **5**, 355 (1908).
[5] *Metallographie*, Vol. I., Part I., p. 953

Selenium-silver.—The system *silver-silver selenide* has been studied by Friedrich and Leroux.[1] A study has

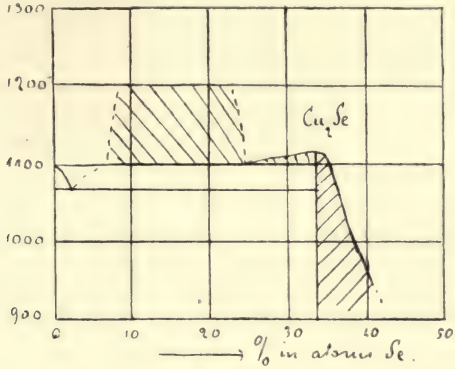

FIG. 181.

also been made by Pellini.[2] Fig. 182 is the diagram constructed by the last named. From the melting point of

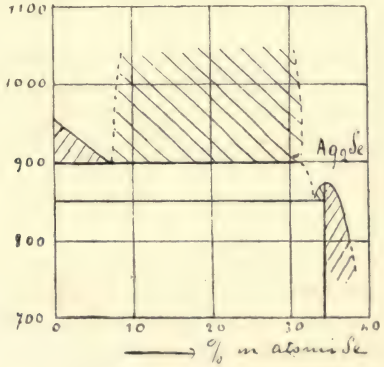

FIG. 182.

selenium (217°) the curve rises rapidly to 696°, and remains horizontal from 5 to 52 per cent. of silver, rising then

[1] *Metall.*, **5**, 355 (1908).
[2] *Gazz. Chim. Ital.*, **45** I., 533 (1915).

to 897° and 66·6 per cent. of silver, the maximum corresponding to the compound Ag_2Se. The curve falls and then rises to 890° and remains horizontal from 68 to 89 per cent. of silver, rising thence to the melting point of the metal. The two horizontal tracts represent gaps in miscibility. At 122° at all concentrations, arrest points are noted which are due to a transformation of the compound Ag_2Se. Pellini performed his experiments in an atmosphere of nitrogen.

Selenium-zinc.—Rio (1828) found a compound $ZnSe_4$ combined with HgS in a mineral from Mexico. Fonces-Diacon (1900) by heating zinc chloride in hydrogen selenide obtained the compound ZnSe in crystalline form.

Selenium-cadmium.—Margottet (1877) obtained from cadmium and hydrogen selenide the compound CdSe, prepared also by Fonces-Diacon (1901).

Selenium-mercury.—This system has been studied by Pellini.[1] The compounds Hg_2Se and HgSe are formed ; the latter can be distilled without decomposition. The highest temperature at which the distillation can be performed is from 600 to 650°. From 500 to 650° the mixture is semi-liquid. From 132° to 139° an arrest is observed due to the solidification of selenium after super-cooling.

Selenium-indium.—According to Thiel and Koelsch (1910) these elements form a compound In_2Se_3. The existence of another compound poorer in selenium is also probable. Indium and selenium mix with a brisk reaction, giving a dark liquid.

Selenium-thallium.—The system has been studied by Pélabon.[2] The compounds Tl_2Se, TlSe and Tl_2S_5 are formed. The fusion curve, leaving the melting point of thallium (302°), runs at first horizontally at 400°. Corresponding to this horizontal tract two liquid layers exist, the lower of pure thallium and the upper a mixture of Tl_2Se and selenium. The curve then falls to an eutectic at 23 per

[1] *Rend. Acc. Lincei*, **18**, II., 211 (1910) ; *Gazz. Chim. Ital.*, **40**, 44 (1910).
[2] *C. R.* **145**, 118 (1907).

cent. of selenium, from which it rises again to 338°, where a maximum corresponding to the compound TlSe occurs. From this maximum the curve falls to the composition of the compound Tl_2S_5, after which there is another horizontal tract at 195°. Here again two liquid layers occur, the upper being a solution of a selenide in selenium and the lower being the selenide Tl_2Se_5.

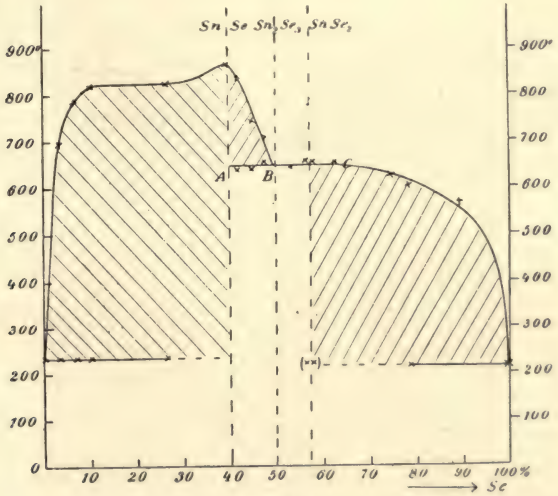

FIG. 183.

Selenium-tin.—The selenides SnSe, Sn_2Se_3 and $SnSe_2$ are known; they were found by Biltz and Mecklenburg [1] in a study of the equilibrium between these elements. The compound SnSe shows a maximum at about 40 per cent. of selenium and 861° (Fig. 183). The second compound occurs at 50 per cent. and 645°, and the third, not well authenticated, at the same temperature and about 57 per cent. of selenium. The curve falls to the left from the maximum at first quickly,

[1] *Zeit. anorg. Chem.*, **64**, 232 (1909).

then slowly, and finally almost vertically to the eutectic, which practically coincides with the melting point of pure tin. On the other side of the maximum the curve, after falling steeply, shows a discontinuity corresponding to the second compound. A more or less horizontal tract then suggests the occurrence of a lack in miscibility.

The eutectic, which crystallises at 217°, is almost pure selenium.

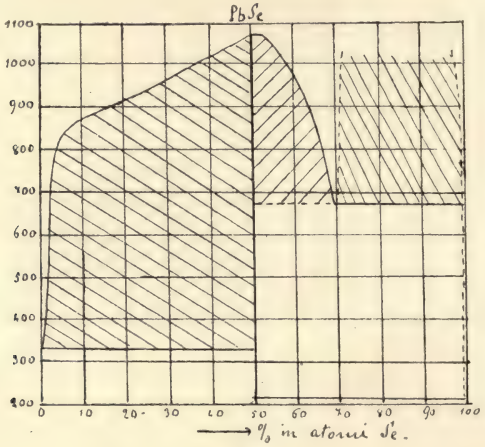

FIG. 184.

Selenium-lead.—The system *lead-lead selenide* has been studied by Friedrich and Leroux [1] and by Pélabon.[2] The melting point of the selenide is very high. According to Friedrich and Leroux it is at 1088°, according to Pélabon at 1065°. From a concentration of 50 per cent., at which the compound is formed, the curve falls continuously to the melting point of pure lead (Fig. 184). Corresponding with the melting point of lead (326°), arrests are noted for all mixtures from 0 to 50 per cent.

[1] *Metall.*, **5**, 355 (1908).
[2] *C. R.*, **144**, 1159 (1897).

Pélabon has investigated the further course of the curve in the region between the selenide and pure selenium. The curve falls to 70 per cent. of selenium, and remains level at 673°, indicating the formation of two strata, the upper of which contains free selenium and the lower the compound. The existence of a compound $PbSe_2$ is not indicated.

Selenium-antimony. Selenium forms with antimony the compound Sb_2Se_3 reported by Pélabon,[1] by Chrétien,[2] who

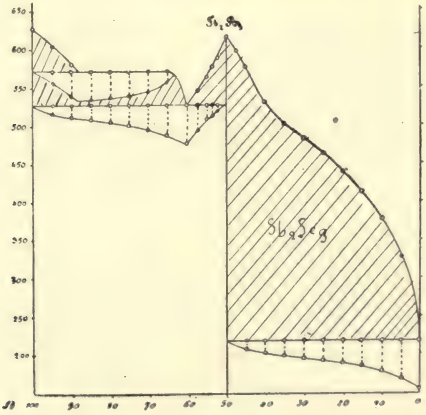

FIG. 185.

mentioned in addition the compounds SbSe, Sb_3Se_4 and Sb_4Se_5, and also by Parravano,[3] who studied the system thermally. The compound (see Fig. 185) separates at 50 per cent. and 630°. It does not mix with antimony in all proportions in the liquid state; two liquid strata occur with 11 and 35 per cent. of selenium respectively. Between 60 and 70 per cent. of selenium a change in direction of the curve indicates, according to Parravano, a lack of miscibility in the liquid state with an upper or lower critical point.

[1] *J. Ch. Phys.*, **2**, 437 (1904); *C. R.*, **142**, 207 (1906).
[2] *C. R.*, **142**, 1339 (1906).
[3] *Gazz. Chim. Ital.*, **43**, I., 210 (1913).

From 50 to 100 per cent. of selenium marked supercooling is observed.

Selenium-bismuth.—Selenium forms two compounds with bismuth, BiSe and Bi_2Se_3, observed by the thermal method through the work of Parravano.[1] The curve (Fig. 186) rises rapidly from the melting point of bismuth up to about 27 per cent. of selenium, where, between 600° and 610°, thermal effects are observed due to the formation of the compound

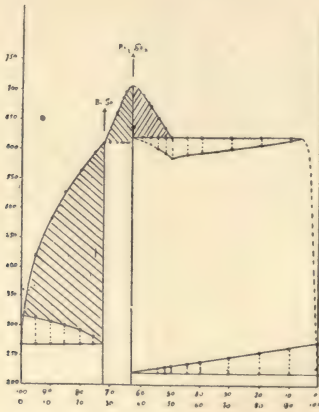

FIG. 186.

BiSe; this is confirmed by microscopical evidence. The curve again rises to 706° and 37 per cent. of selenium and shows a maximum for the compound Bi_2Se. It then descends to about 625°, remains horizontal along a tract and subsequently falls almost vertically to the melting point of pure selenium. The compound Bi_2Se_3 is not completely miscible with selenium; for some mixtures, two liquid layers occur in the liquid state, the lower of which consists mainly of the compound and the upper mainly of selenium.

Selenium-chromium.—Moissan (1880) obtained the com-

[1] *Gazz. Chim. Ital.*, **43**, I., 210 (1913).

pounds Cr_2Se_3 and CrSe by heating chromium chloride in an atmosphere of hydrogen selenide. The existence of these compounds is, however, not well authenticated.

Selenium-manganese.—Fonces-Diacon (1900) obtained the compound MnSe, which, he states, does not decompose on heating.

Selenium-iron.—Fonces-Diacon also prepared the following selenides of iron : Fe_2Se_3, Fe_3Se_4, or Fe_7Se_8 and $FeSe_2$. These on heating are changed into a compound whose composition approximates to the formula FeSe. The homogeneity of this product has not been clearly demonstrated.

Selenium-nickel and *Selenium-Cobalt.* — According to Fonces-Diacon (1900) selenium forms with nickel and cobalt compounds with the following formulæ : M_2Se, MSe, M_3Se_4, M_2Se_3 and MSe_2, where M = Co or Ni. His researches, however, were not founded on the most trustworthy methods.

Selenium-palladium.—Rössler (1895) isolated a selenide, PdSe. An alloy with 6 per cent. of selenium, on treatment with nitric acid, gave a compound with the formula Pd_4Se.

Selenium-platinum.—Rössler also obtained a selenide with the formula PtSe, while Minozzi claimed to have obtained the compounds $PtSe_3$ and $PtSe_2$, the first by precipitating a solution of the double cyanide of platinum and selenium with formaldehyde, and the second by reduction of the first.

Compounds of Tellurium (Tellurides).

Tellurium-copper.—Two compounds are formed, namely, Cu_2Te and Cu_4Te_3. The system has been investigated by Chikashigé [1] ; the diagram is given in Fig. 187. The first compound is formed at 855° at a concentration of about 66·6 per cent. of copper. It separates secondarily in the form of a series of mixed crystals with tellurium from melts containing 100 to 66 per cent. of copper, and primarily from melts with 66 to 50 per cent. of copper. At 623° the last

[1] *Zeit. anorg. Chem.*, **54**, 50 (1907).

species of crystal reacts with the melt of composition *D*, forming the compound Cu_4Te_3. At 365° there is a thermal effect, Cu_4Te_3 being transformed into another crystalline species. Since the maximal arrest occurs at the composition of the compound Cu_4Te_3 it would appear that this is a polymorphic transformation of the compound.

Tellurium-silver.—The compounds Ag_2Te and AgTe are known. Pushin [1] has investigated the system and also

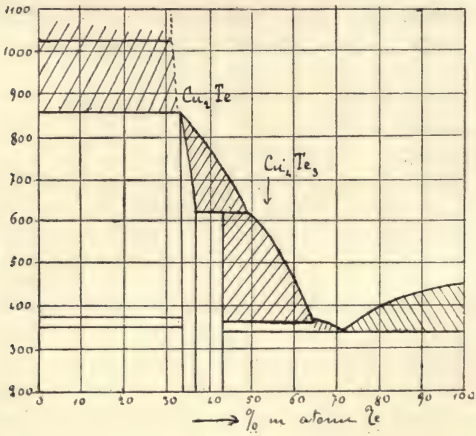

FIG. 187.

measured the electrolytic potential of the alloys of these elements. The system has also been studied by Pellini and Quercigh.[2] Their diagram is shown in Fig. 188. Ag_2Te gives a maximum at 959° and 33·3 per cent. of tellurium. Between this and pure silver an eutectic point is found at 872°. For higher contents of tellurium, *i.e.*, at about 50 per cent., thermal effects are observed at 444° and at 412°, due probably to the compound AgTe. The effect at 412° would appear to be due to a polymorphic transformation of this compound.

[1] *Zeit. anorg. Chem.*, **56**, 8 (1908).
[2] *R. Acc. Lincei*, **19**, II., 415 (1910); *Gazz. Chim. Ital.*, **45**, I., 469 (1915).

Tellurium-gold.—The system has been investigated by Pélabon [1] and by Pellini and Quercigh.[2] The compound

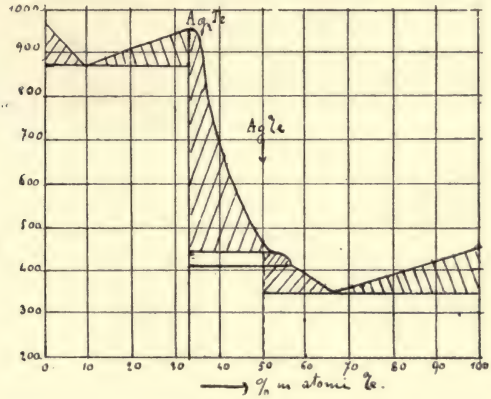

FIG. 188.

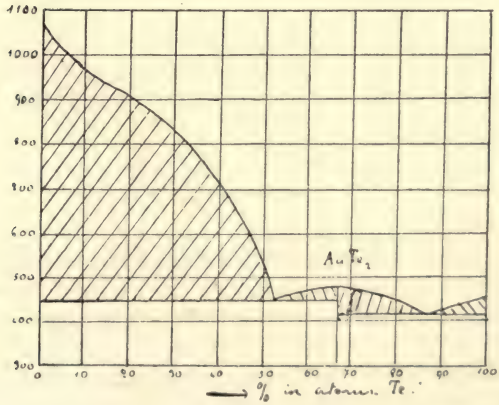

FIG. 189.

$AuTe_2$ occurs, and gives a maximum on the diagram (Fig. 189) at 460° and 66·6 per cent. of tellurium; on both sides of the

[1] *C. R.*, **148**, 1176 (1909).
[2] *R. Acc. Lincei*, **19**, II., 445 (1910).

maximum, eutectics are found, the one with gold at 53 per cent. of tellurium and 450°, and the other with tellurium at 88 per cent. of tellurium and 416°. Solid solutions are formed to a limited extent.

Tellurium-zinc.—Tellurium forms with zinc the compound ZnTe, observed by Kobayaski [1] by means of thermal analysis. It is indicated in the diagram (Fig. 190) by a

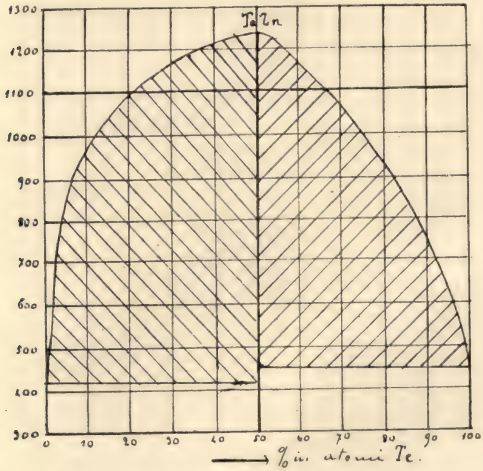

FIG. 190.

maximum at 1238·5°. Complete miscibility exists between the components in the liquid state. The compound TeZn is completely miscible with excess of tellurium in the liquid state, and from these liquid mixtures the compound separates primarily and tellurium secondarily. From liquid mixtures containing excess of zinc, the separation is chiefly of the metal.

Tellurium-cadmium.—The compound CdTe has been recognised. This system has been investigated by Kobay-

[1] *Int. Z. Metall.*, **2**, 65 (1911).

aski.[1] The curve constructed by him (Fig. 191) consists of a single branch, for the eutectics practically coincide with the melting points of the pure components. The compound, in spite of all efforts, could not be obtained in the pure state, nor was it possible to determine with exactitude the temperature and concentration of the maximum. Separation of the compound probably takes place from 50 to 55 per cent. of tellurium and at about 1040°. The cadmium partly

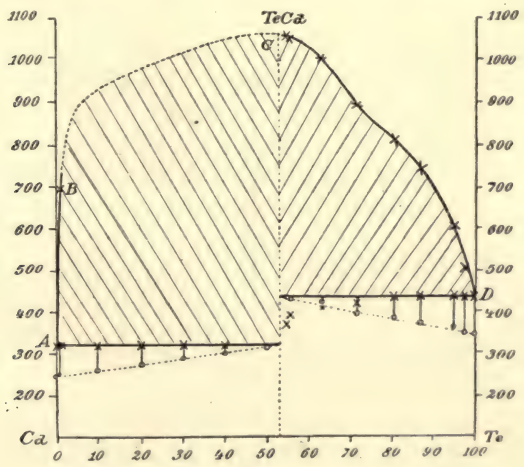

FIG. 191.

volatilises. The alloys from 1 to 2 per cent. of tellurium up to the composition of the compound could not be studied thermally because the components combined with such a great evolution of heat.

Cadmium in the liquid state only dissolves the compound to a small extent, so that a little above 700° a homogeneous melt is only obtained with 0 to 1·2 per cent. of tellurium.

Tellurium-mercury.—According to Pellini,[2] tellurium forms

[1] *Zeit. anorg. Chem.*, **69**, 4 (1911).
[2] *Gazz. Chim. Ital.*, **40**, 46 (1910).

the compound HgTe with mercury. This corresponds to the maximum shown on the diagram (Fig. 192) at 50 per cent. of tellurium and about 610°. The compound forms on the one side an eutectic with tellurium, while on the other it gives a continuous fusion curve down to the melting point of mercury, which means that the eutectic is practically coincident with this point. It is not known certainly whether solid solutions occur.

Tellurium-indium.—According to the investigations of

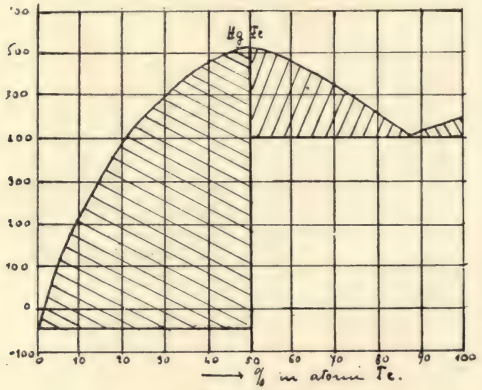

FIG. 192.

Koelsch (1910), these elements when fused together react with evolution of heat. From the analysis of a residue separated out on heating the mixture above 1000° the existence of a compound InTe appears probable.

Tellurium-thallium.—These elements form the compounds Tl_3Te_2 and TlTe. The system has been studied by Chikashigé,[1] and the diagram is shown in Fig. 193. The first compound gives a maximum on the cooling curve at 428° between 27 and 30 per cent. of tellurium ; the second compound is formed at about 305° and 40·5 per cent. of tellurium. At

[1] *Zeit. anorg. Chem.*, **78**, 68 (1912).

200° it forms an eutectic K with tellurium, whose composition is 67·6 per cent. of the compound TeTl and 32·4 per cent. of free tellurium. The eutectic horizontal extends from the ordinate marking the compound TeTl as far as the tellurium axis. Te_2Tl_3 dissolves in thallium, forming a series of mixed crystals. The saturated mixed crystal contains 24 per cent. of tellurium. From 100 to 76 per cent. of tellurium two liquid strata are observed which consist of the fused saturated mixed crystal and fused thallium respectively.

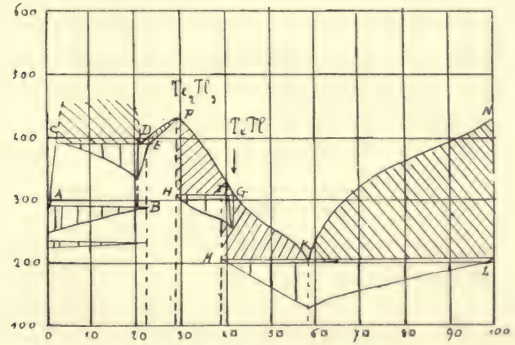

FIG. 193.

TeTl does not form mixed crystals either with the compound or tellurium.

Tellurium-tin.—The compound SnTe has been recognised. The system has been studied by Fay (1907), Biltz and Mecklenburg [1] and Kobayaski.[2] In the diagram (Fig. 194), the compound is indicated by a maximum at 52 per cent. of tellurium and about 800°. From this the curve falls at first steeply, then gradually and again steeply to the eutectic point, which coincides with the melting point of pure tin. Here, as in the case of Sn-S and Sn-Se, two layers occur due to differences in specific gravity and freezing point. On the

[1] *Zeit. anorg. Chem.*, **64**, 233 (1906).
[2] *Ibid.*, **69**, 8 (1911).

other side of the maximum the curve descends rapidly to 404° at 85 per cent. of tellurium, where an eutectic point is found.

Tellurium-lead.—These elements form the compound PbTe. The system has been studied by Fay and Gillson.[1] By addition of tellurium to lead the curve (Fig. 195) rises rapidly to the maximum at 915° which corresponds to the composition of the compound. It then descends to the

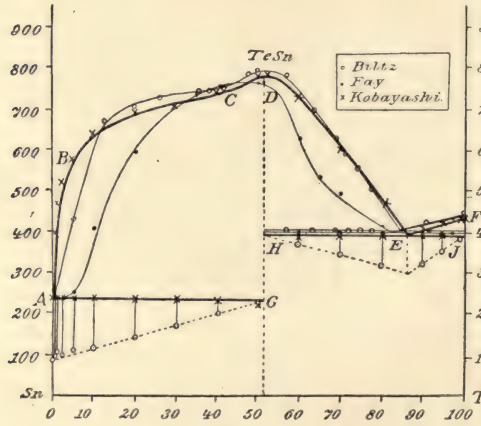

FIG. 194.

eutectic between the compound and tellurium, which is at 400° and 85 per cent. of tellurium. At 322°, on the lead side of the maximum, thermal effects are observed due to secondary crystallisation of pure lead. No eutectic occurs here, or at any rate the eutectic is practically pure lead.

Tellurium-arsenic.—These elements form a compound As_2Te_3. The system was studied by Pélabon,[2] who reports a maximum at 362° and 40 per cent. of arsenic. The data obtained are, however, incomplete and not very reliable.

[1] *Trans. Am. Inst. Min. Eng.*, Nov. 1901.
[2] *C. R.*, **137**, 648; **146**, 1398 (1908).

Tellurium-antimony.—The compound Sb_2Te_3 is known. Studies of the system have been made by Fay and Ashley [1]

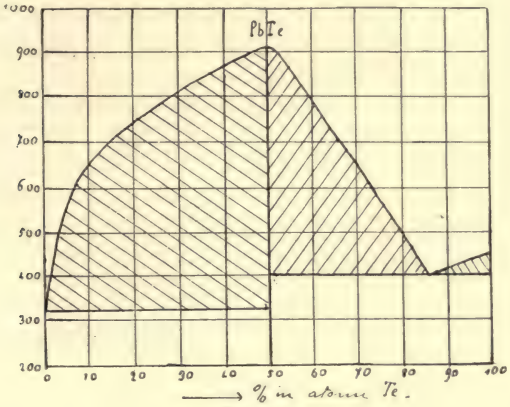

FIG. 195.

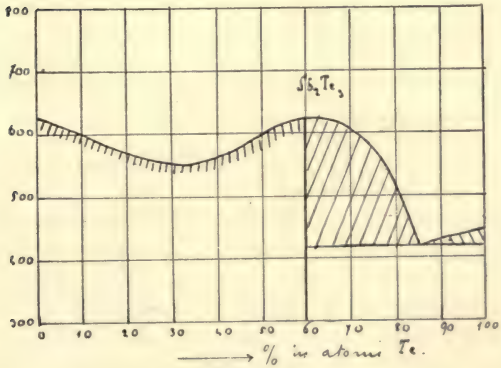

FIG. 196.

and by Pélabon.[2] The diagram (Fig. 196) shows a maximum at 629° and 60 per cent. corresponding to the compounds.

[1] *Amer. Chem. Journ.*, **27**, 95 (1902).
[2] *Ann. Chim. Phys.*, (8), **17**, 539 (1909).

Solid solutions are formed between the compound and antimony. The curve then descends to 427° and 86 per cent. of tellurium, which is an eutectic point. Between tellurium and antimony an extensive range of solid solutions occur. Haken (1910) has carried out measurements of electrolytic potential on these alloys as well as on those of bismuth and tellurium. His data confirm the existence of the compound Sb_2Te_3.

Tellurium-bismuth.—The telluride Bi_2Te_3 is known. The

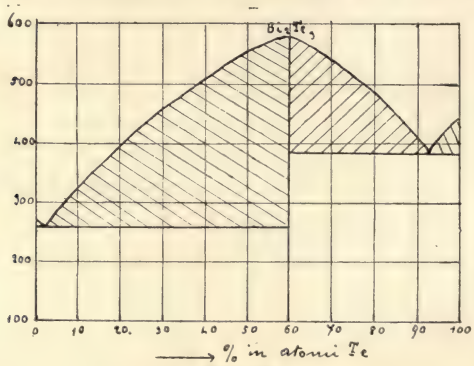

FIG. 197.

system bismuth-tellurium has been investigated by Mönkemeyer [1] and by Pélabon.[2] The diagram constructed by the former is shown in Fig. 197. It is quite simple, showing a maximum at 573° and 60 per cent. of tellurium, corresponding to the compound and two eutectic points, one at 2 per cent. and 261°, and the other at 93 per cent. and 387° The existence of solid solutions has not been established ; the eutectics being so near to the pure components, they could only have a very limited range.

Haken (1910) made measurements of the electrolytic potential and electrical conductivity of these alloys.

[1] *Zeit. anorg. Chem.*, **46**, 419 (1905).
[2] *C. R.*, **137**, 648 (1903) ; **146**, 1397 (1908) ; *Ann. Chim. et Phys.*, (8), **17**, 526 (1909).

Recently G. C. Trabacchi [1] studied the Hall effect in these alloys and obtained curves similar to those of Haken.

Tellurium-iron.—Fabre in 1887 obtained the compound TeFe by direct combination of the elements. Its existence is, however, not well established.

Tellurium-cobalt and *tellurium-nickel.*—Tellurides of the general formula MTe (M = Co or Ni) were obtained by Fabre in 1887, and in 1879 by Margottet. Tibbals (1909) obtained the compound M_2Te_2 $4H_2O$, which on heating was changed by loss of tellurium and water into MTe.

Tellurium-platinum.—The compounds of tellurium and platinum were prepared synthetically by Rössler (1897), who reported the following: $PtTe_2$, PtTe and Pt_2Te. The existence of the last two is, however, doubtful.

[1] *Nuovo Cimento*, (6), **9**, 3 (1915).

CHAPTER VII.

Ternary Intermetallic Compounds.

General Remarks.

The application of thermal methods to the study of intermetallic equilibria has given unlooked-for results, even in systems of more than two components. Up to the present, however, very few ternary intermetallic compounds are known, and even in these cases, the theoretical discussion of their equilibrium diagrams is far from complete. We shall confine ourselves to a brief treatment of this section of our subject, and, although we are here interested mainly in intermetallic compounds, it will be necessary to describe some types in which compounds do not occur. The ternary equilibria are rather obscure from a thermal point of view, and additional complications are introduced by the difficulty of graphic representation, which in such cases often requires a knowledge of the principles of higher geometry.

In the study of a system of three components, A, B and C, it is first of all necessary to understand the three binary systems AB, BC and AC. These being known, the curves belonging to the ternary system are to some extent shadowed forth.

J. W. Gibbs,[1] G. C. Stokes,[2] and Roozeboom [3] have proposed methods for the graphic representation of three component systems ; we shall describe that of Gibbs, which in this kind of work has come into ordinary use. Gibbs represents all the states of equilibrium which can occur in a ternary system by means of an equilateral triangle in which

[1] *Trans. Com. Acad.*, **3**, 176 (1876).
[2] *Proc. Roy. Soc.*, **49**, 174 (1891).
[3] *Zeit. phys. Chem.*, **15**, 147 (1894).

the vertices represent the three components A, B and C. Any point inside the triangle represents a mixture of all three components whose sum is equal to unity, while a point in one of the sides of the triangle represents a binary mixture. Dividing the sides into tenths, we can show the variation in composition of binary mixtures. Similarly, by dividing perpendiculars dropped from the vertices into tenths and drawing a series of lines parallel to the sides, we can define the composition of all possible ternary mixtures. For

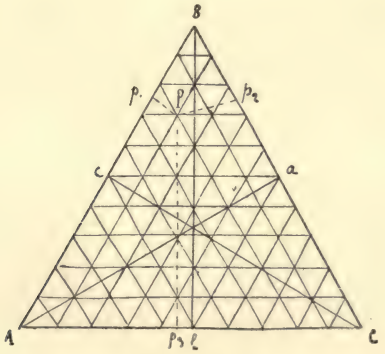

FIG. 198.

example, the point P in Fig. 198 represents a ternary mixture containing ·2 of component A, ·7 of component B, and ·1 of component C, or 20 per cent. of A, 70 per cent. of B and 10 per cent. of C, if 100 be substituted for unity.

If perpendiculars be dropped from any point within an equilateral triangle to the three sides the sum of the lengths of these perpendiculars is equal to the length of a perpendicular from one of the vertices to the opposite side, so that by adopting a suitable scale the composition represented by any point can quickly be found.

As in the case of the binary systems, we shall again reduce the numerous equilibria for three component systems to a

few fundamental types. We may arrange them in three classes :—

Class I.—*The three components crystallise in the pure state without formation of mixed crystals or chemical compounds.*

Class II.—*The three components form mixed crystals but do not combine chemically.*

Class III.—*The three components combine chemically to form either binary or ternary compounds.*

Class I.—The phenomena of crystallisation in ternary

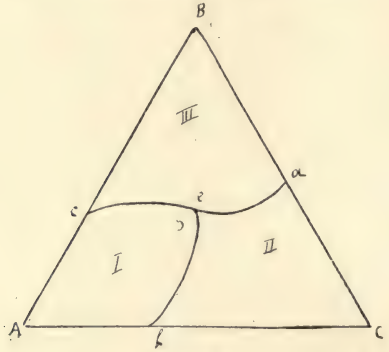

Fig. 199.

systems where the components separate in the pure state have been carefully studied and are well recognised.[1] Using Gibbs' triangular system of representation described above, the most simple case which can be presented is shown in Fig. 199. The diagram is divided into regions I., II. and III.

As was said above, along the sides of the triangle the binary systems which compose the ternary system are indicated ; from these sides the three lines *ae*, *be* and *ce* start and meet in the point *e*, which is the ternary eutectic. The points *a*, *b* and *c* represent the three binary eutectics *B C*, *C A* and *A B*

[1] A system which has been very carefully studied is that of *lead-tin-bismuth*, described by G. Charpy, *C. R.*, **126**, 1569 (1898), and *Bull. Soc. d'Encour.*, (5), **3**, 670 (1898).

respectively. Just as the melting point of a substance is lowered by addition of another substance, so in the case of a binary eutectic the addition of a third substance lowers the melting point until the ternary eutectic is reached which has the lowest melting point of all possible ternary mixtures. At the ternary eutectic point we have the co-existence of three solid phases, one liquid phase and a vapour phase, so that according to the phase rule the system is invariant, or, in

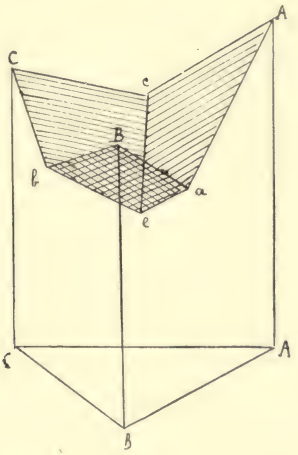

FIG. 200.

other words, all the conditions of this equilibrium are determined.

The nature of the ternary eutectic will be more clearly understood by using a triangular prism instead of an equilateral triangle for the purpose of graphic representation. By this means temperature can be represented as well as composition. In Fig. 200, the binary systems *A B*, *B C* and *C A* have their eutectics in *a*, *b*, and *c* respectively. The fusion curves for these systems are, of course, *A a B*, *B b C* and *C c A* respectively, each lying in a plane formed by one

of the prismatic faces. The curves *a e*, *b e* and *c e*, which show how the eutectic point of a binary system is lowered by addition of a third component, are called the ternary eutectic curves. Three plane surfaces meet in the ternary eutectic point ; they represent the bivariant equilibria of one component and a liquid phase. The ternary eutectic curves represent monovariant equilibria, while the ternary eutectic point, as was said above, represents a non-variant system.

A section parallel to the base of the prism will, of course, give an isotherm of the system.

Class II.—The equilibria of ternary systems in which solid solutions occur are exceedingly complicated, and their discussion would carry us beyond the limits imposed on this work. The problem is of great interest, although, since the existence of ternary compounds has only been observed in a few cases, it has not a direct bearing on our subject. The problem is often rendered more complex by the occurrence of gaps in the isomorphism of the components. Systems in which ternary mixtures exhibit complete isomorphism have been studied by Schreinemakers,[1] Jänecke,[2] and Parravano and Sirovitch.[3] When one considers the numerous cases which can exist in binary systems in which isomorphous mixtures are present, the complicated nature of ternary systems with occurrence of isomorphous mixtures is only to be expected.

Class III.—In this class of ternary equilibria we meet complications. We shall discuss a few possible cases which will arise according as one or two binary compounds appear or as a ternary compound is formed. The last case is the most interesting for our subject as it enables us to throw some light on the formation of ternary compounds.

Type I.—*Of the three components, completely miscible in the liquid state, two, A and B, form a binary compound D.* We

[1] *Zeit. phys. Chem.*, **52**, 513 (1905).
[2] *Ibid.*, **67**, 641 (1909).
[3] *Gazz. Chim. Ital.*, **41**, I., 417, 478, 569, 621 (1911) ; **42**, I., 417 (1912). Also N. Parravano, *ibid.*, I., 220 (1913).

shall assume for the sake of simplicity that no solid solutions occur and that the binary compound melts without decomposition. Figs. 201 and 202 indicate the character of the diagram, using the method of graphic representation explained above. In both diagrams the points K_1 and K_2 respectively are the two ternary eutectic points ; we have in equilibrium the solid phases A, B and D, together with a liquid phase at the one point and the solid phases B, C and D and a liquid phase at the other point. The crystallisation

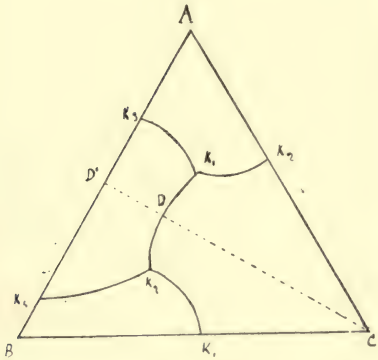

FIG. 201.

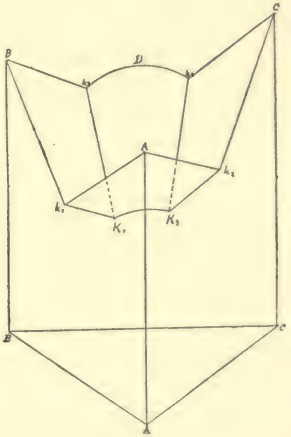

FIG. 202.

in such liquid mixtures occurs as in the binary mixtures of pure substances.

TYPE II.—*Of the three components, completely miscible in the liquid state, A and B form a compound D, and A and C form a compound E.*

As in the preceding case, we shall exclude the formation of mixed crystals. The equilibrium diagram is shown in Fig. 203. After what has been said with regard to the preceding case, the crystallisation along the line $D'E'$ is worth notice. The crystallisation processes for the various mix-

tures of D and E can be compared to those occurring in a binary system of two components which form an eutectic, and which, though completely miscible in the liquid state, do not form mixed crystals. As we shall see in the description of the ternary system *magnesium-aluminium-zinc*, this part of the diagram often serves to indicate whether or not a ternary compound occurs.

TYPE III.—*The three components are completely miscible in the liquid state, A and B form a compound D, A and C form a compound E, and B and C form a compound F.*

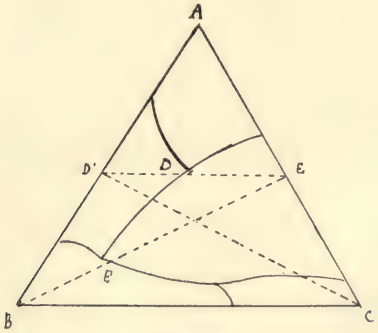

FIG. 203.

If solid solutions do not occur and the compounds melt without decomposition, the diagram can be represented by Fig. 204. Four ternary eutectics will occur, three of which will represent the equilibrium of two compounds and a pure component, while the fourth will represent the equilibrium of the three compounds.

TYPE IV.—*The three components form a ternary compound.* Excluding the formation of mixed crystals and of binary compounds, and supposing that the components are completely miscible in the liquid state, this type is represented by the diagram shown in Fig. 205. A number of eutectics occur. Three binary eutectics, a, b, and c, lie on the sides

of the triangle. There will also be three eutectics lying along the lines joining E to the corners of the triangle

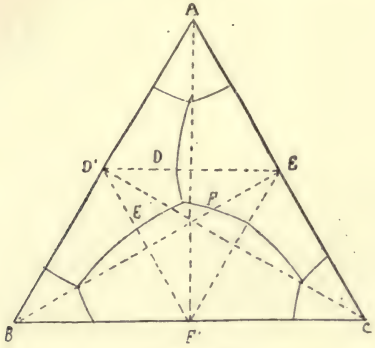

FIG. 204.

and three eutectics between these and the binary eutectics a, b and c.

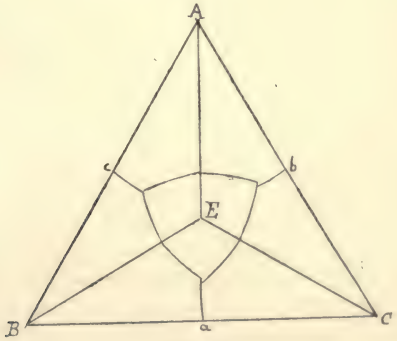

FIG. 205.

Sodium-potassium-mercury. Sodium-cadmium-mercury.—The study of these systems has been carried out by Jänecke,[1] but the results are not as yet decisive. In any case

[1] *Zeit. phys. Chem.*, **57**, 507 (1907).

Jänecke has been able to demonstrate the presence of a chemical compound in each of these systems. The compounds show the following characteristics: (1) a homogeneous crystalline structure when viewed under the microscope; (2) a definite melting point; (3) all alloys having concentrations slightly different from that of the compound have a lower melting point.

Jänecke's curve shows that marked super-cooling takes place. The compound $NaKHg_2$ crystallises in shining hexagonal prisms of a steel blue colour and is oxidised on exposure to air. Its melting point is 188°, while that of NaHg is 217° and that of KHg 178°. By addition of KHg the melting point of the ternary compound may be lowered about 18°, and by addition of NaHg about 5°; further addition of these substances leads to a rise in melting point. A lowering is, however, produced by sodium or potassium, or by amalgams containing more of these metals than the binary compounds mentioned.

The compound NaCdHg which separates in crystals of the regular system melts at 325°, as compared with 350° for $NaHg_2$ and 380° for $NaCd_2$. Addition of the latter two compounds lowers the melting point of NaCdHg by about 20°.

Magnesium-aluminium-zinc. — The system has been studied by Eger.[1] The diagram was constructed by means of a number of sections perpendicular to the fundamental concentration plane. The first section is the line joining the points representing the compounds Al_3Mg_4 and Zn_3Mg on the diagram; the diagram is thus divided into two parts —on the one hand the quadrilateral Al-Al_3Mg_4-Zn_2Mg-Zn and on the other the triangle Al_3Mg_4-Mg-Zn_2Mg. The melting point of each binary compound is lowered by addition of the other, and an eutectic point occurs at 450° and 15 per cent. Zn, 37·5 per cent. Al and 47·5 per cent. Mg. The extent of the eutectic horizontal indicates the occurrence

[1] *Int. Z. f. Metall.*, **4**, 50 (1913).

of mixed crystals. At the eutectic point two kinds of mixed crystals are in equilibrium with the melt. A series of arrests at 505° show a maximum at 61 per cent. Zn, 12·5 per cent. Al and 26·5 per cent. Mg.

In addition to the two components Zn_3Mg and Al_3M_4g

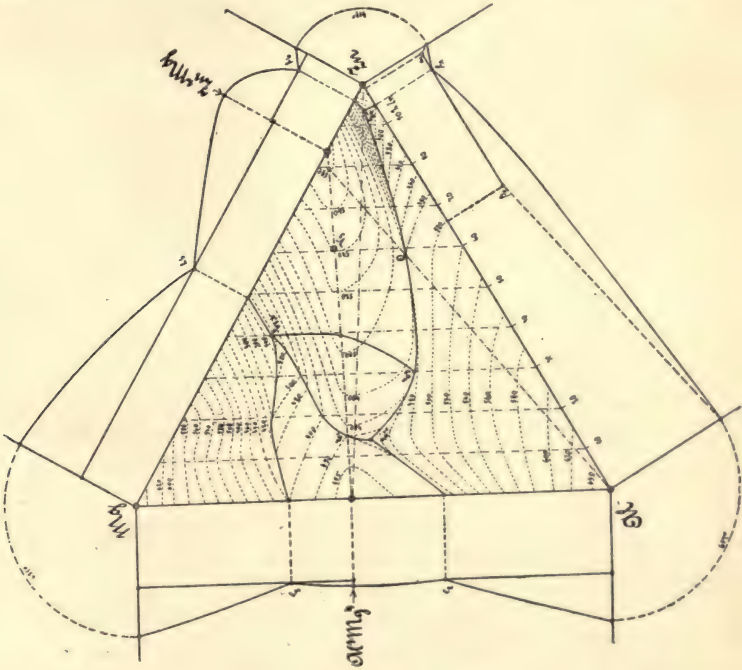

FIG. 206.

a third phase exists with an obscured maximum. The compound of the formula $Zn_6Al_3Mg_2$ melts at 505° with decomposition.

$$Zn_6Al_3Mg_7 \rightleftarrows \text{melt A} + \text{mixed crystals B.}$$

Melts of composition approaching that of $MgZn_2$ separate another series of crystals.

Micrographic study was not possible on account of the hardness and brittleness of the two binary compounds. The equilibrium diagram in the region Al_3Mg_4-Zn_2Mg-Zn-Al comprises a convex surface of primary solidification. Near to the point indicating pure zinc there are two eutectic points and a transformation point.

In the region Mg-Al_3Mg_4-Zn_2Mg, the ternary compound does not form mixed crystals; the eutectic practically coincides with the peritectic point.

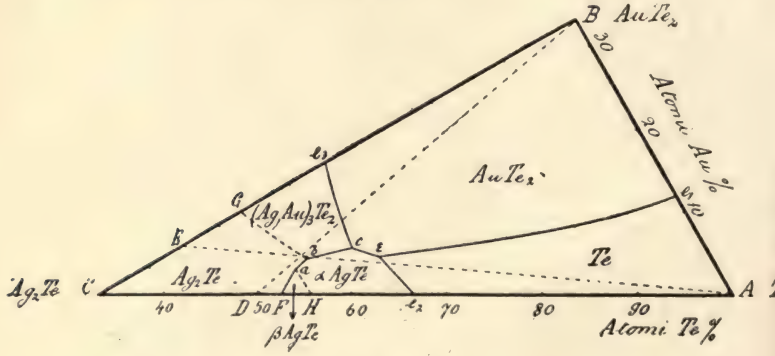

FIG. 207.

Silver-gold-tellurium. — This system has recently been investigated by Pellini,[1] who has directed his researches in particular to the system Ag_2Te-$AuTe_2$-Te and succeeded in defining the compound $(AgAu)_3Te_2$, in which gold partly replaces silver. The experimental study of this system presented difficulty, for the thermal phenomena were not always well defined. The diagram is reproduced in Fig. 207. The ternary compound does not separate directly, but melts with decomposition. The points *a*, *b*, *c*, *e* on the diagram represent nonvariant equilibria. The investigation of all the states of equilibrium in this system is by no means

[1] *Gazz. Chim. Ital.*, **45**, I., 469 (1915).

complete, and the complications which occur in the binary systems comprised in it vastly increase the difficulties of thermal investigation.

The possibility of the formation of ternary compounds of silver, gold and tellurium seems evident when it is considered that such compounds occur naturally. Gastaldi [1] has recently described such a compound, to which he gives the formula $(AgAu)_2Te_5$.

These ternary combinations of course belong to the group of heteropolar compounds. If they result from the union of dissimilar atoms, the partial substitution of an electropositive element by another closely related element is always possible. No other ternary combinations have as yet been deduced from the study of equilibrium diagrams. From the physico-chemical point of view these compounds are only known to a very small degree owing to the lack of systematic researches, as is the case in so many binary combinations.

[1] *Rend. Acc. Sci. Fis. e Nat. di Napoli* (3), **17**, 22 (1911).

Melting Points and Atomic Weights of the more important Metals and Metalloids.

Element.	Symbol.	Atomic weight.	Melting point. Deg. C.
Aluminium	Al	27·1	658·7
Antimony	Sb	120·2	630·5
Arsenic	As	75·0	850 (?)
Barium	Ba	137·4	850·0
Beryllium	Be	9·1	1278·0
Bismuth	Bi	208·0	271·0
Boron	B	11·0	2000—2500 (?)
Cadmium	Cd	112·4	320·9
Calcium	Ca	40·1	800 ca.
Carbon	C (diamond)	12·0	> 3600 ca.
Cerium	Ce	140·25	> 800
Cæsium	Cs	132·9	26
Cobalt	Co	59·0	1480
Chromium	Cr	52·1	1520
Copper	Cu	63·6	1084·1
Gallium	Ga	70·0	30
Gold	Au	197·2	1063·5
Indium	In	115·0	155
Iridium	Ir	193·0	2350 (?)
Iron	Fe	55·9	1530
Lanthanum	La	138·9	810 (?)
Lead	Pb	206·9	327·4
Lithium	Li	7·03	186
Magnesium	Mg	24·36	635
Manganese	Mn	55·0	1260
Mercury	Hg	200·0	— 38·9
Molybdenum	Mo	96·0	2500 (?)
Nickel	Ni	58·7	1451
Osmium	Os	191·0	2700 (?)
Palladium	Pd	106·5	1549
Phosphorus	P	31·0	I. 44—II. 930
Platinum	Pt	194·8	1780
Potassium	K	39·15	62·5
Rubidium	Rb	85·5	38
Ruthenium	Ru	101·7	2450 (?)
Selenium	Se	79·2	217
Silicon	Si	28·4	1420
Silver	Ag	107·93	961·5
Sodium	Na	23·5	97·5
Sulphur	S	32·6	I. 112·8—II. 119·2 III. 106·2
Strontium	Sr	87·6	> Ca, < Ba (?)
Thallium	Tl	204·1	302
Tellurium	Te	127·6	450
Tin	Sn	119·0	232
Titanium	Ti	48·1	1800
Tungsten	W	184·0	> 3000
Uranium	Ur	238·5	< 1850
Vanadium	V	51·2	1720
Zinc	Zn	65·4	419

Periodic System of the Elements.

Series.	Group O.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
	—	—	—	—	RH_4	RH_3	RH_2	RH	
	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
1		H = 1·008							
2	He = 4·0	Li = 7·03	Be = 9·1	B = 11·0	C = 12·0	N = 14·01	O = 16·0	F = 19·0	
3	Ne = 20·0	Na = 23·05	Mg = 24·36	Al = 27·1	Si = 28·4	P = 31·0	S = 32·06	Cl = 35·45	
4	A = 39·9	K = 39·14	Ca = 40·1	Sc = 44·1	Ti = 48·1	V = 51·2	Cr = 52·1	Mn = 55·0	Fe = 55·9, Ni = 58·7 Co = 59·0
5		Cu = 63·6	Zn = 65·4	Ga = 70·0	Ge = 72·5	As = 75·0	Se = 79·2	Br = 79·96	
6	Kr = 81·8	Rb = 85·5	Sr = 87·6	Y = 89·0	Zr = 90·6	Nb = 93·7	Mo = 96·0		Ru = 101·7 Rb = 103·0 Pd = 106·5
7		Ag = 107·93	Cd = 112·4	In = 115·0	Sn = 119·0	Sb = 120·2	Te = 127·6	I = 126·97	
8	Xe = 128·0	Cs = 132·9	Ba = 137·4	La = 138·9	Ce — Yb* 140·25–173·0	Ta = 181·0	W = 184·0		Os = 191·0, Ir = 193·0, Pt = 194·8
9		Au = 197·2	Hg = 200·0	Tl = 204·1	Pb = 206·9	Bi = 208			
10			Ra = 225		Th = 232·5		U = 238·5		

* Ce—Yb include the following elements:—Praseodymium = 140·5, Neodymium = 143·6, Samarium, 150 : 3, Terbium = 160·0, Erbium = 166·0, Ytterbium = 173·0.

Binary Systems Studied Thermally.

(*Homopolar Combinations.*)

	Na	K	Rb	Cs	Cu	Ag	Au	Be	Ca	Mg	Zn	Cd	Hg	Al	In	Tl	Sn	Pb	Ce	Sb	Bi	Cr	Mo	Mn	Fe	Ni	Co	Pd	Pt
Li	O	O	—	—	—	—	—	—	—	O	—	C	C	—	—	—	C	—	—	—	—	—	—	—	—	—	—	—	—
Na		C	—	—	—	O	C	—	—	O	C	C	C	O	—	C	C	C	—	C	C	—	—	—	—	—	—	—	—
K			—	—	—	—	—	—	—	O	C	C	C	O	—	C	C	C	—	C	C	—	—	—	—	—	—	—	—
Rb				—	—	—	—	—	—	—	—	—	C	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cs					—	—	—	—	—	—	—	—	C	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cu						O	O	e	C	C	C	C	—	C	—	O	C	O	—	C	O	O	—	O	O	O	O	O	O
Ag							O	—	C	C	C	C	—	C	—	O	C	O	—	C	O	O	—	C	O	O	O	O	C
Au								—	—	C	C	C	—	C	—	O	C	C	—	C	O	—	—	C	O	O	O	O	
Be									—	—	—	—	—	O	—	—	—	—	—	—	—	—	—	—	C	—	—	—	
Ca										C	C	C	C	C	—	C	C	C	—	C	C	—	—	—	—	—	—	—	
Mg											C	C	C	C	—	C	C	C	C	C	C	—	—	—	C	—	—	—	
Zn												O	O	O	—	O	O	O	—	C	O	C	—	C	C	C	C	—	
Cd													O	O	—	O	O	O	—	C	O	C	—	—	C	C	C	—	
Hg														—	C	C	O	O	—	—	O	—	—	—	—	—	—	—	
Al															—	O	O	O	C	C	O	C	—	C	C	C	C	—	
In																O	—	O	—	—	—	—	—	—	—	—	—	—	
Tl																	—	C	—	C	C	—	—	O	O	O	O	—	C
Sn																		O	C	C	O	O	—	C	C	C	C	—	C
Pb																			C	O	O	O	—	O	O	O	O	C	C
Ce																				—	C	—	—	—	—	—	—	—	—
Sb																					O	C	—	C	C	C	C	C	C
Bi																						O	—	C	O	C	O	—	—
Cr																							—	—	C	C	O	—	—
Mo																								—	C	C	C	—	—
Mn																									O	O	O	—	—
Fe																										C	C	—	O
Ni																											O	O	—
Co																												—	—
Pd																													O

C = *Chemical combination.*

O = *Absence of chemical combination.*

— = *No thermal study made up to the present.*

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